HYDROGEN-HEAVY HYDROCARBON PHASE EQUILIBRIA AND MODELING OF A RECIRCULATION REACTOR

By

HUAPING CHEN

Bachelor of Engineering

East China Institute of

Chemical Technology

Shanghai, P. R. China

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Thesis Approved:

Mayis Seapan

Thesis Adviser

Arland H. Johannes

Ruth A. Allen

Norman N. Durham

Dean of the Graduate College

PREFACE

Four aspects of a Berty reactor were studied in this work. a - The flow uniformity of a vapor-liquid mixture in the reactor was studied by visual observation. A uniform flow of the two-phase mixture could be obtained only when the reactor is operated in a batch mode. In the continuous flow mode a uniform flow pattern inside the reactor could not be observed even at the highest magnedrive speed. b - The reactor liquid holdup was measured under different operating conditions in both transient and steady state modes and the results were used to develop correlations to predict the liquid holdup in a Berty reactor. c - A computer program was developed to predict the phase behavior of a multicomponent hydrogen-heavy hydrocarbon system. The binary experimental data were used to obtain the interaction parameters. The validity of the results and that of the mixing rule was checked against experimental ternary data. The results were extended to predict the phase behavior of a multicomponent system, specifically that of hydrogen/Tetralin/cis-decalin /trans-decalin mixture. d - The reactor startup at elevated temperatures and pressures was modeled using a transient material balance combined with the liquid holdup correlations and phase equilibrium calculation results. Overall a technique was developed to simulate the unsteady state

behavior of a type reactor at high temperatures and pressures.

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CHAPTER I

INTRODUCTION

Berty reactor is an internal recirculation reactor widely used in laboratory research (1). Because of its capability of producing kinetic data free from bulk phase mass and heat transfer effects (2), it is also known as a gradientless reactor. Berty et al. (3) illustrated that perfect mixing and gradientless state could be reached by increasing magnedrive rotator speed when circulating fluid was a single gas or vapor phase. Many researchers (4) have used the Berty reactor for kinetic study and catalyst testing of gas phase system. When the reaction fluid is a vapor-liquid mixture, however, only a few reports can be found in the open literature in which a Berty reactor was used for kinetic study and catalyst testing (1,5). None of these studies has addressed the dynamics of flow in the reactor and only one has reported the nonuniformity of flow in the reactor (1).

A Berty reactor was used for kinetic study of several catalytic hydrogenation processes in this laboratory (1,5,6). From these studies, it was realized that the flow uniformity and phase equilibrium were two major factors affecting the effective use of the Berty reactor and interpretation of the

experimental data.

The objective of this project is therefore to study the dynamics of flow of a two phase vapor-liquid mixture inside a Berty reactor and to predict the phase behavior of multicomponent hydrogen and heavy hydrocarbon mixtures at elevated temperatures and pressures.

In studying the flow uniformity of a vapor-liquid two phase mixture, visual observations were conducted and a series of pictures was taken. The observations were conducted at ambient temperatures and low pressures while the inlet liquid and gas flow rates and magnedrive speed were systematically varied. It was found that uniform flow of two phase mixture could not be reached in Berty reactor whenever it was operated as a continuous flow reactor. When the reactor was operated in batch mode, however, uniform flow of two phase mixture could be reached when magnedrive speed exceeded 1000 rpm. The change in inlet liquid flow rate and pressure did not produce an appreciable change in the flow uniformity. The change in inlet gas flow rate affected the bubbling rate but had no effect on the flow uniformity. The liquid holdup was defined as the total amount of liquid circulating inside the reactor. The liquid holdup was measured at different operating conditions for developing the correlations needed in modeling the reactor start-up process.

In predicting the phase condition of hydrogen and heavy hydrocarbons mixtures at elevated temperatures and pressures,

reliability of the prediction technique and calculation efficiency require good accuracy and efficiency in prediction of K-values of each component involved. This was achieved by using an equation of state approach. Binary interaction parameters were obtained from fitting binary experimental data at different temperatures. These interaction parameters were then tested on some ternary systems for which experimental data were available. Calculation showed that the fitted interaction parameters from binary data could be directly used in the K-value prediction of ternary systems with good accuracy. These binary interaction parameters were then tabulated and used in multicomponent isothermal flash calculations. From isothermal flash calculations, the phase condition could be predicted at different inlet liquid and gas flow rates for a given system temperature and pressure.

Finally, correlations were developed for estimating the liquid holdup in the reactor at its transient and steady state operation. A mathematical model was developed to simulate the start-up process of the reactor at elevated temperatures and pressures. From this simulation, the transition points from one phase to two phase and thus phase boundary were identified. Furthermore, a procedure was developed to estimate the steady state liquid holdup at elevated temperatures and pressures.

CHAPTER II

LITERATURE REVIEW

This literature review will cover the following subjects:

1. Berty reactor
2. Vapor-liquid equilibrium calculation of hydrogen and heavy hydrocarbon mixtures

Berty Reactor

The Berty reactor is an internal recirculation reactor in which a fixed catalyst bed is placed in the center of the reactor body. A stirrer which consists of a magnedrive and an impeller is mounted through the bottom of the reactor and circulates the reaction fluid inside the reactor. The reaction fluid moves upwards from the bottom of reactor, outside the catalyst basket and changes direction at the top cover of the reactor to downwards, due to concave shape of the reactor cap, then passes through the catalyst basket.

Designed initially to study gas phase catalytic reactions, Berty et al. (3) reported a detailed evaluation of this reactor when circulating fluid is a gas. It was indicated that by proper selection of a minimum magnedrive speed, a uniform flow with uniform mixing in bulk phase could

be achieved and the temperature and concentration gradients outside the catalyst particles could be eliminated or minimized. Thus the Berty reactor has been regarded as a gradientless reactor.

Berty (7) reported a preliminary hydrodynamic study of the reactor in which a liquid and gas mixture was used as reaction fluid. Without giving any information about the operation of reactor, it was claimed that a good circulation or flow pattern could be obtained when magnedrive speed was 800 rpm. It was further claimed that the Berty reactor was also good when circulating fluid was a gas-liquid mixture.

On the contrary, Robinson et al. (2) indicated that the Berty reactor or other similar reactors where the catalyst bed was fixed in the center of the reactor body was not appropriate for kinetic study when the circulating fluid was a two phase mixture. Once again, no detailed information is released for making such a conclusive remark.

To investigate the potential usage of the Berty reactor for kinetic study where reaction fluid would be a two phase mixture, a 300 ml Berty reactor was used in the kinetic study of different hydrogenation processes in this laboratory(1,6). In these studies, it was found that the reactant conversion had a maximum value when magnedrive speed was varied from 1000 to 2000 rpm. The maximum conversion occurred at 1500 rpm. It was also found that the catalyst coking was completely non-uniform. Here, the question arose whether or

not the two phase reaction fluid inside the reactor had a uniform flow over the catalyst bed.

It is therefore intended in this project to make a hydrodynamic study of the Berty reactor when the circulating fluid is a liquid-vapor mixture. Three problems will be addressed. The first is if it is possible to reach a uniform flow over the catalyst bed. The second is how to reach the uniform flow condition. The third is which operating parameters affect the flow uniformity and how.

Vapor-Liquid Equilibrium Calculation Of Hydrogen And Heavy Hydrocarbon Mixtures

From a previous study in this laboratory (1), it was found that the vapor phase hydrogenation reaction of Tetralin was significant compared to the liquid phase reaction at elevated temperatures and pressures. Therefore, to conduct a kinetic study of a catalytic hydrogenation process in a well defined phase, the vapor-liquid phase equilibrium of the reaction system must be known. Since both hydrogen and a mixture of heavy hydrocarbons are usually involved in hydrogenation of heavy oils, it is therefore intended in this project to model the vapor-liquid phase behavior of hydrogen and heavy hydrocarbon mixtures.

Due to the importance of vapor-liquid equilibria of hydrogen and heavy hydrocarbons in the process development of utilizing heavy fossil fuels, many researchers have become

involved in this subject since late 1970s.

There are virtually two approaches available in modeling vapor-liquid phase equilibria. One is using the activity correlation procedure, the other is using the equation of state approach. In modeling vapor-liquid equilibrium of hydrogen containing mixtures, almost every researcher has used the equation of state approach in order to avoid complexity introduced by the supercritical state of hydrogen at most circumstances. In selecting the appropriate equation of state, the Redlich-Kwong (8) and its two modifications made by Soave (9) and Peng-Robinson (10) have frequently been used by various researchers because of their simplicity and good performance.

The Redlich-Kwong equation can be written as:

$$P = \frac{R\,T}{V - b} - \frac{a}{T^{0.5}\,(V+b)\,V} \qquad \text{II-1}$$

where, a and b are two parameters which, according to Redlich-Kwong can be calculated by the following relations :

$$a = 0.42748\,\frac{(R\,T_C)^2}{P_C}\,\frac{1}{T_r^{0.5}} \qquad \text{II-2}$$

$$b = 0.08664\,\frac{R\,T_C}{P_C} \qquad \text{II-3}$$

where, P, T, V and R are pressure, temperature, molar volume

and gas constant respectively. The subscript c refers to the critical state. Tr is the reduced temperature expressed as :

$$Tr = T / T_c \qquad \text{II-4}$$

Soave (9) modified the Redlich-Kwong equation of state by writing the equation of state as:

$$P = \frac{R\,T}{V - b} - \frac{a}{V\,(V + b)} \qquad \text{II-5}$$

where a and b can be calculated by the following relations :

$$a = 0.42748 \frac{(R\,T_c)^2}{P_c}\,\alpha \qquad \text{II-6}$$

$$b = 0.08664 \frac{R\,T_c}{P_c} \qquad \text{II-7}$$

$$\alpha^{0.5} = 1 + m\,(1 - T_r^{0.5}) \qquad \text{II-8}$$

$$m = 0.48 + 1.574\,W - 0.176\,W^2 \qquad \text{II-9}$$

where W is the acentric factor of the fluid.

Peng - Robinson equation of state (10) has the following form:

$$P = \frac{R\,T}{V - b} - \frac{a}{V(V+b)+b(V-b)} \qquad \text{II-10}$$

where a and b can be calculated by the following relations :

$$a = 0.457235 \frac{(R T_C)^2}{P_C} \alpha \qquad \text{II-11}$$

$$b = 0.077796 \frac{R T_C}{P_C} \qquad \text{II-12}$$

$$\alpha^{0.5} = 1 + m (1 - T_r^{0.5}) \qquad \text{II-13}$$

$$m = 0.37646 + 1.54226 W - 0.26992 W^2 \qquad \text{II-14}$$

When an equation of state is used for a mixture, a mixing rule is needed. Among various mixing rules so far proposed, the classic one fluid mixing rule is frequently used :

$$a_m = \Sigma \Sigma X_i X_j a_{ij} \qquad \text{II-15}$$

$$b_m = \Sigma \Sigma X_i X_j b_{ij} \qquad \text{II-16}$$

where,

$$a_{ij} = (1.0-C_{ij}) (a_i a_j)^{0.5} \qquad \text{II-17}$$

$$b_{ij} = 0.5 (1.0+D_{ij}) (b_i + b_j) \qquad \text{II-18}$$

and C_{ij}, D_{ij} are interaction parameters usually obtained from fitting or regressing the binary experimental data.

A.I.El-Twaty (11) studied the correlation of K-values for mixtures of hydrogen and heavy hydrocarbons. In using the Soave-Redlich-Kwong equation of state, the composition

dependence of the parameter b for the mixture was modified. The modification introduced a binary parameter which had a physically reasonable size and good results were obtained for seven hydrogen-heavy hydrocarbon binaries.

Graboski and Daubert (12) modified Soave-Redlich-Kwong equation of state in their phase equilibrium calculation by introducing a new expression for α of hydrogen and subsequently eliminating the need for the interaction parameters. Nineteen binaries were studied using this procedure in which both light and heavy hydrocarbons were covered.

Gray et al. (13) used Joffe-Zudkevitch (14, 15) modification of Redlich-Kwong equation along with the one fluid mixing rule and local mixing rule of Huron-Vidal (16) form to predict the vapor-liquid equilibrium of hydrogen containing multicomponent systems. It was found that the interaction parameter in one fluid mixing rule was strongly temperature dependent and only could be very roughly correlated. Also it was found that certain deficiencies existed in the local mixing rule in the prediction of heavy hydrocarbon solubility in compressed gases. As a continuous effort of a research group at Exxon Research and Engineering Company, Tsonopoulos (17) later reported that use of two interaction parameters in the one fluid mixing rule generally did not show any improvement on the vapor-liquid equilibrium prediction of hydrogen containing systems.

Moysan (18) studied the predication of solubility of hydrogen in hydrocarbon solvents. Both Soave-Redlich-Kwong and Peng-Robinson equations of state were used. The interaction parameters were obtained from experimental data including Henry's constant. The interaction parameter could be correlated as a simple function of temperature regardless of the nature of solvent.

Chokappa and Streett (19) reported their procedure in predicting phase equilibrium of hydrogen containing systems using perturbation theory. However, the binary systems that they covered were limited to hydrogen with light gases only.

Valderrama (20) studied the vapor-liquid equilibrium of hydrogen-containing mixtures by using Peng-Robinson equation of state along with one fluid mixing rule. In this procedure, the mixture parameters and pseudocritical constants were evaluated by regressing experimental data and a final correlation was obtained for the interaction parameter.

Laugier et al. (21) compared the different means of representing vapor-liquid equilibrium data for hydrogen-hydrocarbon mixtures by examining the perturbed hard chain equation of Gmehling (22), Soave-Redlich-Kwong equation and three of its modifications. Gmehling's equation of state was found to be the most accurate one for representing the phase equilibrium.

Radosz (23) studied high pressure vapor-liquid equilibria of asymmetric systems which included hydrogen and

heavy hydrocarbon mixtures. The proposed procedure used the original Soave-Redlich-Kwong equation of state incorporating a modified mixing rule which was in fact a simplified form of the conformal solution theory. As a final result, the interaction parameters were correlated by the acentric factor of the hydrocarbon.

Mathias (24) introduced a purely empirical parameter called polar factor into the correlation of α for hydrocarbons and meanwhile an exponential form was used for α of hydrogen. The original form of Soave-Redlich-Kwong equation of state was retained in the procedure. The interaction parameter was correlated with temperature and solubility data.

In a recent paper, Han et al. (25) reviewed the application of equations of state in vapor-liquid equilibrium calculation for several types of mixtures including hydrogen containing mixtures. They concluded that Soave-Redlich-Kwong equation, Peng-Robinson equation, Kubic (26) equation and Cubic-Chain-Of-Rotators (27) equation gave overall comparable results while Heyen (28) equation was not adequate for hydrogen mixtures.

At elevated temperature and pressure ranges, there are two ternary systems comprised of hydrogen and heavy hydrocarbon components for which experimental data are available (29). But only one of them so far has been modeled. Gray et al. (13) modeled hydrogen / Tetralin /

diphenylmethane system by using the interaction parameters obtained from hydrogen / Tetralin and hydrogen / diphenylmethane binary system. However, It was indicated that proper modification of binary interaction parameters fitted from binary experimental data was needed before these parameters could be used in ternary calculations.

Overall, the equation of state approach in modeling vapor-liquid equilibrium of hydrogen containing mixtures is the preferred approach. Various modification have been made both on the mixing rule and the attractive term of the two-parameter equation of Redlich-Kwong type. Various modification generally produce better prediction of vapor-liquid phase behavior of hydrogen and heavy hydrocarbon mixture but calculation procedure generally becomes more complicated. Furthermore, only a few researchers have tested their results obtained from binary system on ternary systems, which actually serves as a test of the generality and the applicability of these procedures.

Base on the available information on modeling vapor-liquid equilibrium of heavy hydrocarbon and hydrogen mixtures, a strategy is developed in this project to address the requirement of prediction of phase condition. First, the equation of state approach is adopted to make the vapor-liquid phase equilibrium calculation efficient. Second, binary experimental data is used to fit for the optimum interaction parameters. Third, the calculated interaction

parameters are then used in K-value prediction on two ternaries. Fourth, after verifying the validity of the procedure with the ternary systems, the interaction parameters are tabulated and used in multicomponent isothermal flash calculations to predict the phase condition for a four component system of hydrogen / Tetralin / cis-decalin / trans-decalin.

CHAPTER III

EXPERIMENTAL APPARATUS AND HYDRODYNAMIC STUDY

Experimental Apparatus

A schematic process flow diagram (1) of the hydrogenation system is shown in Figure 1 and the internal structure of the Berty reactor (1) is shown in Figure 2.

The liquid feed is continuously pumped into the reactor by a Milton Roy positive displacement pump. The pump pressure is monitored by a pressure gauge. The liquid volumetric flow rate is metered through feed tank which is a graduated buret cylinder with a maximum capacity of 500 ml and in increments of 5 ml. The maximum liquid flow rate is about 5 ml per minute and the desired liquid flow rates can be adjusted by the micrometer of the pump within its limits. A check valve is positioned between the pump exit and the reactor inlet to prevent any back flow from the reactor.

The hydrogen or nitrogen is supplied from gas cylinders. The gas pressure is regulated by a Victor 2-stage regulator. Passing through a rotameter, the gas flow rate is controlled and set to the desired level by adjusting valve V15. A cold trap is in the gas line before the reactor to prevent hydrocarbons from diffusing back into the gas line.

Both the liquid and gas are fed into the reactor through

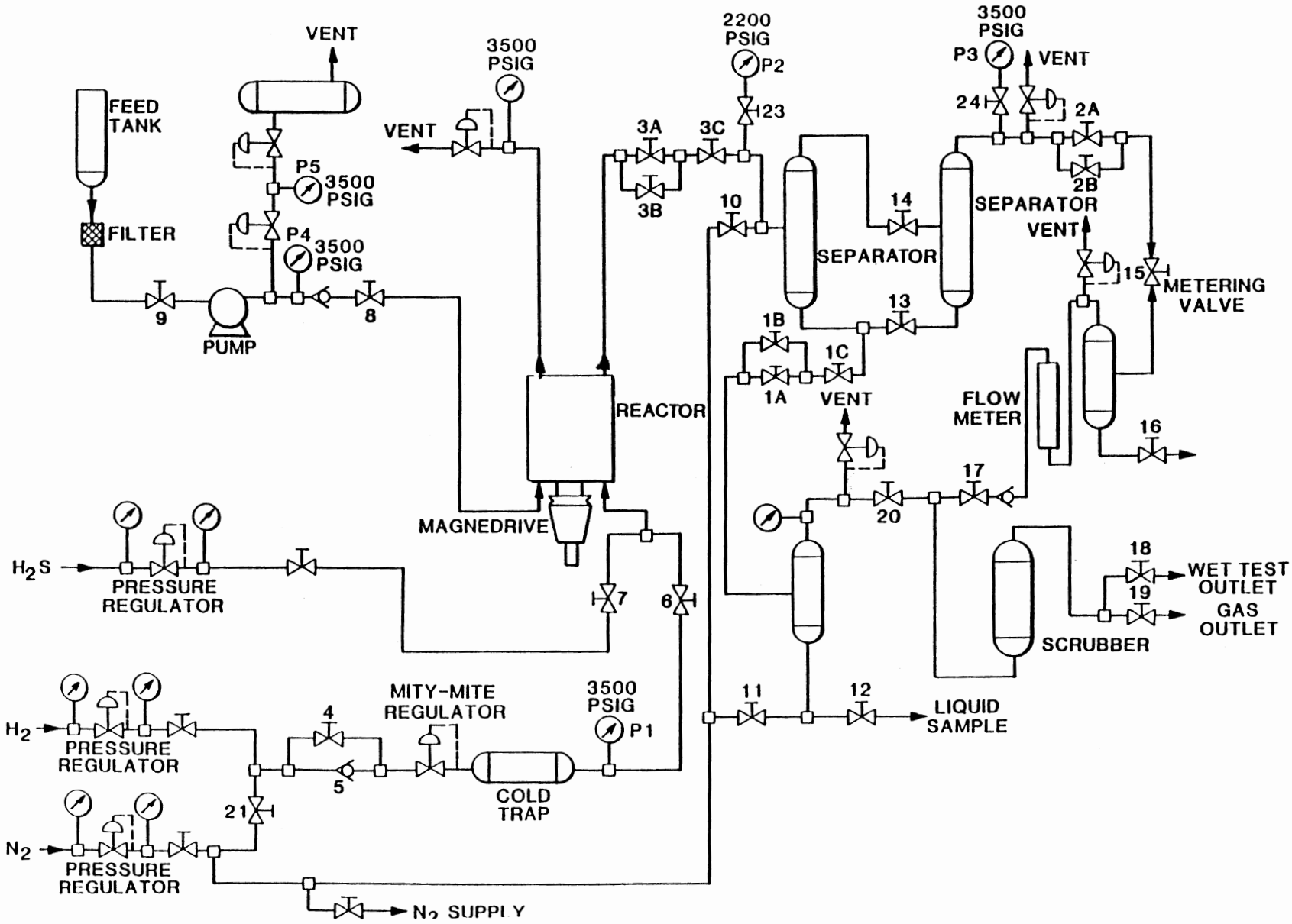

Figure 1. Schematic System Flow Diagram (1)

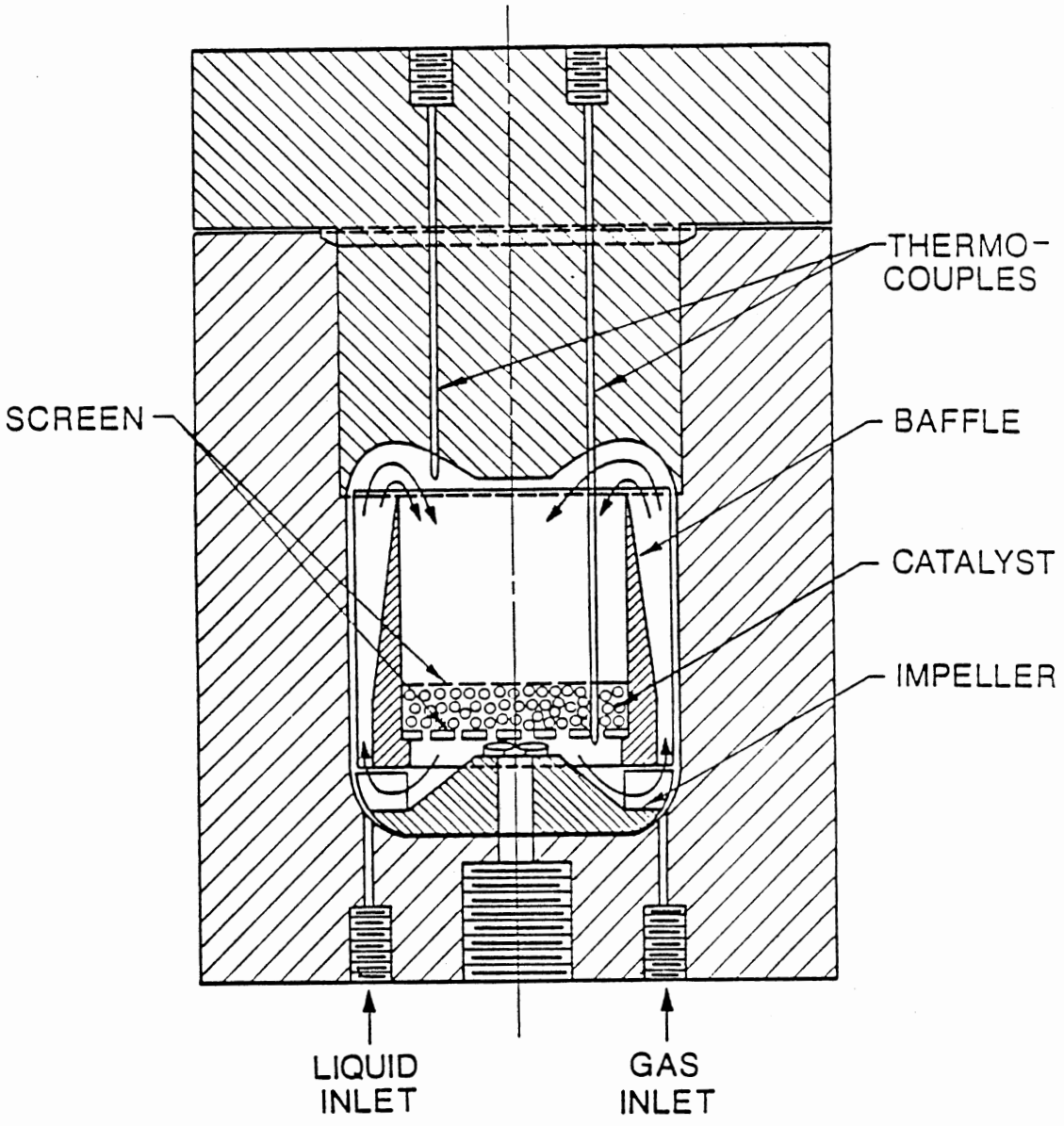

Figure 2. Internal Structure of the Berty Reactor (1)

its bottom without pre-mixing. The gas-liquid mixture exits the reactor from the port located on the cap of the reactor. They are then separated at the two consecutively positioned separation cylinders. The outlet liquid can be collected and sampled at the third cylinder. After passing through a scrubber, the outlet gas can be either vented or further connected to a wet test meter. The temperature can be controlled by an Autoclave Engineers temperature controller. Two thermocouples (both J-type) are placed inside the reactor to measure the temperature of the solid phase and the flowing fluid phase respectively. The stirrer is driven by an Autoclave Engineers Magnedrive-II with a Maximum allowable working pressure of 24.4 mPa and a maximum speed of 3000 rpm.

Visual Observation of Flow Patterns

A plexiglass reactor cap was constructed with the same dimensions of the real reactor cap except for a small difference in the curvature at the inner surface of the plexiglass cap because of the machining difficulty of the material. The visual observations were made by replacing the stainless steel reactor cap with the plexiglass one. Operating conditions such as magnedrive speed, gas flow rate, liquid flow rate and pressure were varied and a series of pictures were taken after the system reached its hydrodynamic steady state. All the visual observations were conducted at room temperature. A total of four flow patterns with clear

differences were observed. The results of the visual observation are documented and discussed in Chapter VI.

Measurement of the Liquid Holdup

In order to measure the liquid holdup, defined as the total liquid accumulated inside the reactor, the plexiglass reactor cap was replaced by the stainless steel reactor cap. Then, the liquid and gas were fed into the reactor. After the desired liquid and gas flow rates were stabilized, the stirrer was started. After a selected short period of time, the inlet and outlet lines of the reactor were shut off simultaneously and the pump and magnedrive were turned off. The total liquid pumped into the reactor and the total liquid accumulated in the separation cylinders were measured. The difference between these two quantities was taken as the total liquid accumulated inside reactor at that moment. For measuring the liquid holdup at hydrodynamic steady state, the reactor was brought back on line and the previous procedure was repeated several times until there was no significant difference between the liquid holdups measured. A graduated cylinder with a capacity of 50 ml and increments of 1 ml was used for all the liquid volume measurement. The results of the measurement of the liquid holdup are documented and discussed in Chapter VI. The detailed experimental procedure is given in Appendix A.

CHAPTER IV

VAPOR-LIQUID EQUILIBRIUM CALCULATION OF HYDROGEN AND HEAVY HYDROCARBON MIXTURES

Vapor-liquid phase equilibrium calculation of hydrogen and heavy hydrocarbon mixtures can be roughly grouped into four parts:

1. Calculation of the Parameters for Equation of State
2. Binary Data Fitting
3. Testing on Ternary System
4. Multicomponent Isothermal Flash Calculation

Calculation of the Parameters for Equation of State

The original equation of state proposed by Redlich-Kwong (8) is used in this project (Eq. II-1). Because the critical property data of heavy hydrocarbons are not usually available or the available data are not accurate, the procedure of Joffe-Zudkevich (14, 15) is adopted in this project for calculation of $\underline{a}$ and $\underline{b}$, the two parameters of Redlich-Kwong equation of state for heavy hydrocarbon components.

The main point of Joffe-Zudkevich procedure is to get the values of $\underline{a}$ and $\underline{b}$ by fitting the pure component vapor pressure and liquid density along the saturated liquid

isotherm. The calculated a and b are assumed to be applicable to the vapor phase at the saturated condition. Detailed description of this procedure can be found from Zudkevich et al (14, 15). In this project, a computer program for calculation of a and b for heavy hydrocarbon components was developed on an IBM PC model XT in FORTRAN. Details of the calculation procedure and its explanation can be found in Appendix B. The calculation flow chart and the computer program codes are given in Appendix C.

For hydrogen, neither Equation II-2 and II-3 nor Joffe-Zudkevich procedure can be used to calculate a and b, because of the quantum effect of the hydrogen molecule. According to Chueh (30), the following equation are used to calculate the a and b for hydrogen :

$$a = 0.42748\ R^2\ T_C^{2.5} / P_C \qquad \text{IV-1}$$

$$b = 0.0866\ R\ T_C / P_C \qquad \text{IV-2}$$

$$T_C = 43.6 / (1 + 10.9 / T) \qquad \text{IV-3}$$

$$P_C = 20.2 / (1 + 22.1 / T) \qquad \text{IV-4}$$

where, T_C and P_C are the effective critical temperature and critical pressure of hydrogen with the unit ^{o} K and atm respectively. T is the temperature in unit ^{o} K.

The ten hydrocarbons considered in this project are listed in Table I along with the sources of correlations or data of vapor pressure and density of pure hydrocarbon

TABLE I

SATURATED VAPOR PRESSURE AND DENSITY CORRELATION SOURCES USED IN CALCULATION OF PARAMETERS OF EQUATION OF STATE

Pure Component Name	Temperature Range (oC)	Vapor Pressure Correlation	Liquid Density Correlation
Tetralin	10 - 447	(31)	(31)
9,10 Dihydro-phenanthrene	164 - 279	(32)	(33)
n-Hexadecane	127 - 447	(32)	(33)
m-Xylene	59 - 344	(32)	(33)
1-Methylnaph-thalene	142 - 499	(32)	(33)
Cyclohexane	20 - 280	(32)	(33)
m-Cresol	150 - 433	(32)	(33)
n-Decane	95 - 345	(32)	(33)
Diphenyl-methane	189 - 429	(32)	(33)
Tolune	36 - 319	(32)	(33)

components.

Binary Data Fitting

In conjunction with the Redlich-Kwong equation of state, the classic one fluid mixing rule is used with two simplified forms (Equation II-15 to Equation II-17):

First case :

$$D_{ij} = 0 \qquad \text{IV-5}$$

Second Case :

$$C_{ij} = 0 \qquad \text{IV-6}$$

In one fluid mixing rule, C_{ij} and D_{ij} are two interaction parameters which can be obtained by either regressing or fitting binary experimental data. In this project, all the interaction parameters for the ten binaries (See Table II) are obtained from fitting the binary experimental data. The main point of the data fitting is to select the one interaction parameter which minimizes the following object function:

$$F = \left(\sum_{i}^{N} (X_i \phi_i^{L} - Y_i \phi_i^{V})^2 \right) / N \qquad \text{IV-7}$$

at system bubble point condition. Calculation results are documented in CHAPTER VI for ten binary systems in two cases either C_{ij} or D_{ij} is kept as zero.

TABLE II

BINARY HYDROGEN CONTAINING SYSTEMS

Identification Number	Binary System	Pressure Range(atm)	Temperature Range(^{o} C)	Source of Data
1	Tetralin	20 - 250	189 - 389	(34)
2	9,10-Dihydronathren	20 - 250	189 - 269	(35)
3	n-Hexadecane	20 - 250	189 - 391	(36)
4	m-Xylene	20 - 250	189 - 309	(37)
5	1-Methylnaphthalene	20 - 250	189 - 429	(38)
6	Cyclohexane	30 - 620	70 - 138	(39)
7	m-Cresole	20 - 250	189 - 389	(37)
8	n-Decane	20 - 250	189 - 310	(40)
9	Diphenylmethane	20 - 250	189 - 429	(41)
10	Toluene	20 - 250	189 - 302	(42)

Detailed calculation procedure and its explanation are given in Appendix B. The computer program and its flow sheet are given in Appendix C.

Testing of Ternary Systems

The ultimate goal of this modeling work is to utilize the interaction parameters of the binary systems to predict the phase behavior of multicomponent systems, specifically that of hydrogen / Tetralin / cis-decalin/ trans-decalin. Since no experimental data could be found for this system, the validity of the technique will be tested on ternary systems first.

The ternary experimental data of hydrogen and heavy hydrocarbon mixtures under elevated temperature and pressure conditions are scarce. Experimental data could be found only for hydrogen / Tetralin / diphenylmethane and hydrogen / Tetralin / m-xylene. The purpose of this test is to check if it is necessary to modify the interaction parameters obtained from the binary data fitting when they are used in ternary or multicomponent system. The calculation results and a discussion are presented in CHAPTER VI.

Multicomponent Isothermal Flash Calculation

A computer program for multicomponent isothermal flash calculation was developed. In order to avoid non-convergence, options of using either terminal input or Wilson's

correlation to make initial estimates of the component K-values are provided. Options are also provided to avoid making flash calculation in a single phase. Detailed calculation procedure and explanation are given in Appendix B. Computer program and calculation flow sheet are given in Appendix C.

Typical calculation results (C_{ij} is kept non-zero and D_{ij} equal to zero) for a hydrogen / Tetralin / cis-decalin / trans-decalin four components system are documented in CHAPTER VI. This quartery system covers the major components existed in the reaction system which was extensively studied in the Berty reactor in our laboratories (1,5,6).

CHAPTER V

SIMULATION OF THE START-UP OF THE REACTOR

A mathematical model is developed to simulate the start-up process of a Berty reactor at elevated temperatures and pressures. The system is assumed to be non-reactive. With the purpose to obtain the analytical rather than numerical solution to the model, the system is assumed to have two components, One is the hydrocarbon and the other is hydrogen. The procedure developed in this chapter can be easily extended to a multicomponent system using a numerical method when necessary. However, as one will see the analytical result obtained using the binary system can be used as a good approximation for the multicomponent system.

The start-up of the reactor for hydrogenation process usually begins with the reactor filled with hydrogen at a high temperature and pressure. Hence the start-up process can be viewed as a two step process. First step is the rapid evaporation of the liquid hydrocarbon pumped into the reactor while the reactor is operated at pure vapor phase condition. The second step is the accumulation of the liquid mixture after the vapor phase inside the reactor reaches its dew point. Obviously, for very low liquid feed rates at high temperatures a special case may occur, in which a liquid

phase can never form inside the reactor. Thus the reactor will be operated in the vapor phase.

Since the dew point is in fact a transition point across which the reactor system changes from a single vapor phase to a liquid and vapor two phase system, the start-up of the reactor therefore can be viewed as a phase transition process. By incorporating the phase equilibrium calculation, the developed mathematical model addresses three problems. a - the existence of the dew point or the transition point. b - the time required for the reactor to reach the dew point or transition point. c - The time needed for the reactor to reach its hydrodynamic steady state. These are accomplished by (1) modeling the unsteady state single vapor phase process (2) modeling the unsteady state liquid accumulation process and (3) correlating steady state liquid holdup.

Modeling The Unsteady State Single Vapor Phase Process

Perfect mixing of the vapor phase inside the Berty reactor is both desirable and attainable for kinetic study. It is therefore assumed that the vapor phase is perfectly mixed. Furthermore, compressibility factor of the vapor phase is assumed to be a constant at a fixed reactor temperature and pressure. This results in :

$$\frac{d\,Z}{d\,t} = 0$$

where, Z is the compressibility factor of the vapor phase and t is the time elapsed after the feeds are pumped into the reactor. The material balance for the reactor at the unsteady state gives :

$$M_{HCIN} = \frac{d\,(C_{HC}\,V_F)}{d\,t} + \frac{C_{HC}}{C_{H2}}\,M_{H2OUT} \qquad V\text{-}1$$

$$M_{H2IN} = \frac{d\,(C_{H2}\,V_F)}{d\,t} + M_{H2OUT} \qquad V\text{-}2$$

$$C_{H2} + C_{HC} = \frac{P}{Z\,R\,T} = C \qquad V\text{-}3$$

where, M_{HCIN}, M_{H2IN}, M_{H2OUT} are inlet hydrocarbon molar flow rate, inlet hydrogen molar flow rate and outlet hydrogen molar flow rate respectively. V_F is the free volume inside the reactor or the volume taken by the vapor phase inside the reactor. C_{HC}, C_{H2} and C are hydrocarbon molar concentration, hydrogen molar concentration and overall molar concentration of the vapor phase. Since the temperature and pressure are fixed during the start-up process and the compressibility factor, Z, is assumed constant, Eq. V-3 gives:

$$\frac{d\,C_{HC}}{d\,t} = -\frac{d\,C_{H2}}{d\,t} \qquad V\text{-}4$$

By combining Eq. V-1 and Eq. V-2 :

$$M_{HCIN} = \frac{d\,(C_{HC} V_F)}{d\,t} + \frac{C_{HC}}{C_{H2}}\left[M_{H2IN} - \frac{d\,(C_{H2} V_F)}{d\,t} \right] \qquad V\text{-}5$$

Combine Eq. V-3 , Eq. V-4 and Eq. V-5 :

$$M_{HCIN} = - V_F \frac{d\,(C_{H2})}{d\,t} + \frac{C - C_{H2}}{C_{H2}}\left[M_{H2IN} - V_F \frac{d\,C_{H2}}{d\,t} \right] \qquad V\text{-}6$$

Rearrange Eq. V-6 :

$$M_{HCIN} = \frac{C - C_{H2}}{C_{H2}} M_{H2IN} - \frac{C V_F}{C_{H2}} \frac{d\,C_{H2}}{d\,t} \qquad V\text{-}7$$

Multiply Eq. V-7 with C_{H2} :

$$C_{H2} M_{HCIN} = (C - C_{H2}) M_{H2IN} - C V_F \frac{d\,C_{H2}}{d\,t} \qquad V\text{-}8$$

Rearrange Eq. V-8 using Eq. V-3 :

$$\frac{d\,C_{H2}}{d\,t} = \frac{M_{H2IN}}{V_F} - \frac{(M_{H2IN} + M_{HCIN})}{C\ V_F} C_{H2} \qquad V\text{-}9$$

Rearrange Eq. V-9 by introducing :

$$\tau = \frac{C\ V_F}{M_{H2IN} + M_{HCIN}}$$

$$R_M = \frac{M_{HCIN}}{M_{H2IN}}$$

where, τ is the reactor space time and R_M is the molar feed ratio of hydrocarbon to hydrogen. Rewrite the Eq. V-9 using τ and R_M to get :

$$\frac{d\,C_{H2}}{d\,t} = -\frac{C_{H2}}{\tau} + \frac{C}{\tau\,(R_M + 1)} \qquad V\text{-}10$$

Defining dimensionless time t^* and hydrogen molar fraction Y_{H2} as :

$$t^* = \frac{t}{\tau}$$

$$Y_{H2} = \frac{C_{H2}}{C}$$

Then following equation is obtained :

$$\frac{d\,Y_{H2}}{d\,t^*} = -Y_{H2} + \frac{1}{R_M + 1} \qquad V\text{-}11$$

Let further define a parameter which will be called as the reactor limited hydrogen molar fraction in the vapor phase :

$$Y_{H2LT} = \frac{1}{R_M + 1}$$

The Y_{H2LT} represents the hydrogen mole fraction when time goes to infinity as will be seen later.

Then Eq. V-11 becomes :

$$\frac{d\,Y_{H2}}{d\,t^*} = -\,Y_{H2} + Y_{H2LT} \qquad \text{V-12}$$

if $Y_{H2} = Y_{H2}^{\,O}$ at $t^* = 0$

Then solution of Eq. V-12 is :

$$t^* = -\,Ln\,\frac{Y_{H2} - Y_{H2LT}}{Y_{H2}^{\,O} - Y_{H2LT}} \qquad \text{V-13}$$

Expressing the Eq. V-13 in terms of R M and τ gives :

$$\frac{t}{\tau} = -Ln\,\frac{(1+R_M)\,Y_{H2} - 1}{(1+R_M)\,Y_{H2}^{\,O} - 1} \qquad \text{V-14}$$

Eq. V-14 gives the relation of the change of the hydrogen mole fraction with time while the R_M and $Y_{H2}^{\,O}$ serve as two parameters which relate to the process conditions. Clearly, the effect of different process conditions on the existence of the transition point and the corresponding time needed to reach this transition point can be readily assessed by

incorporating phase equilibrium calculation.

From Eq. V-14, it is obvious that Y_{H2} decreases exponentially with the time elapsed. Since the dew point of the system is fixed at a specified temperature, pressure and inlet feed rates, Y_{H2} can gradually approach its dew point molar fraction and stop there without any further change. However, if the hydrogen mole fraction at dew point is such that Y_{H2} from Eq. V-14 can never reach the dew point mole fraction, then Y_{H2} will gradually approach Y_{H2LT} as its limit. If Y_{H2} can reach the system dew point, then liquid will start to accumulate inside the reactor and the start-up process goes into two phase region as discussed next.

Modeling the Unsteady State Liquid Accumulation Process

After the dew point is reached, the liquid starts to accumulate inside the reactor. The liquid accumulation is an unsteady state process and will continue until a hydrodynamic steady state is reached. As stated previously, hydrodynamic steady state refers to a state under which liquid holdup inside the reactor will not change.

From experimental study of liquid entrainment during the unsteady state liquid accumulation process, it is found that total liquid entrained by exit gas is always less than 5 ml (See Chapter VI). Therefore, it is assumed that no liquid is entrained from the reactor during the entire unsteady state

liquid accumulation process. This assumption is equivalent to that all the liquid fed into the reactor during this process is 'used' to increase the liquid holdup inside the reactor. Hence one can get :

$$H(t) = Q_{LIN}\, t \qquad \text{V-15}$$

where t is the time elapsed after the dew point is reached and Q_{LIN} is the liquid flow rate. At room temperature and ambient pressure Q_{LIN} is equal to the liquid feed rate. At high temperatures and pressures, however, Q_{LIN} in Eq. V-15 should be replaced by the flow rate of liquid mixture after flashing at reactor temperature and pressure provided the assumption is still valid at high temperature and high pressure. Q_{LIN} at a high temperature and pressure can be obtained by a flash calculation at the fixed temperature, pressure and feed rates and it therefore represents the combined effects of temperature, pressure and feeds rate on the liquid accumulation process. A comparison of calculation results with the experimental measurements for one typical liquid accumulation process is presented in CHAPTER VI.

Correlating The Steady State Liquid Holdup

Liquid accumulation process ends when a steady state liquid holdup is reached. This steady state liquid holdup can be measured easily if the reactor is operated at room temperature and ambient pressure condition as described in

Chapter III. At high temperatures and pressures, direct measurement of the steady state liquid holdup is extremely difficult if not impossible. Because the steady state liquid holdup is required to calculate the time needed to reach steady state, a procedure is developed to closely estimate it as shown below.

Under Elevated Temperatures and Pressures

At steady state, the total hydrocarbon inside the reactor can be calculated as :

$$MOL_{HC} = Y_{HC} (V_F - H) C_V + X_{HC} H C_L \qquad V\text{-}16$$

where, MOL_{HC} is the total moles of one hydrocarbon component. Y_{HC} and X_{HC} are the mole fraction of the hydrocarbon component at vapor phase and liquid phase respectively. H is the liquid holdup.

Rearrange the above equation one gets :

$$H = \frac{MOL_{HC} - Y_{HC} V_F C_V}{X_{HC} C_L - Y_{HC} C_V} \qquad V\text{-}17$$

Replace C_V and C_L with corresponding liquid and vapor specific molar volumes $1 / V_V$ and $1 / V_L$:

$$H = \frac{MOL_{HC} V_V V_L - Y_{HC} V_F V_L}{X_{HC} V_V - Y_{HC} V_L} \qquad V\text{-}18$$

The quantities of MOL_{HC} and V_F can be measured

after the reactor is cooled down and the pressure is released. All the other quantities can be calculated from the vapor-liquid phase equilibrium calculation. Thus Eq. V-18 provides an alternative way to estimate the actual liquid holdup at high temperatures and pressures. Some calculation results are presented in CHAPTER VI for the hydrogen / Tetralin binary non-reactive mixture.

Under Ambient Temperatures and Pressures

Since the above developed procedure for estimation of steady state liquid holdup relies partly on the experimental study, it becomes useless when one is required to estimate the steady state liquid holdup before conducting any experiment at a given set of operation conditions. Thus a correlation for estimating steady state liquid holdup is necessary.

Based on the experimental study of steady state liquid holdup at different operation conditions (See CHAPTER III), a correlation is proposed to have the form :

$$H = a\, N^{b}\, Q_{GIN}^{c}\, Q_{LIN}^{d} \qquad \text{V-19}$$

where, N is the magnedrive speed with the unit rpm, Q_{GIN} and Q_{LIN} are inlet gas and liquid flow rates with the unit ml/min while a, b, c and d are empirical parameters.

To obtain the parameters of the Eq. V-19, it is first transformed into the following form :

$$\log H = \log a + b \log N + c \log Q_{GIN} + d \log Q_{LIN} \qquad V\text{-}20$$

Using the standard multiple variable least square regression technique (43) and the first five sets of the experimental results (See Table III), the following values of parameters are obtained :

a = 144.431

b = 0.00036

c = -0.06487

d = 0.05997

therefore, the empirical correlation can be written as :

$$H = 144.43\ N^{0.00036}\ Q_{GIN}^{-0.06487}\ Q_{LIN}^{0.05997} \qquad V\text{-}21$$

Because the parameter b is very small it can be neglected without introducing any significant error. Since the absolute values of the parameter c and d are almost equal to 0.06, therefore, the correlation is simplified to the following form :

$$H = e \left(\frac{Q_{LIN}}{Q_{GIN}} \right)^{k} \qquad V\text{-}22$$

The e and k are obtained by regressing again and the results are :

$$H = 145.06 \left(\frac{Q_{LIN}}{Q_{GIN}} \right)^{0.0676}$$

This correlation covers the following operating range :

5.0	>	Q_{LIN}	>	0	ml/min
1125	>	Q_{GIN}	>	250	ml/min
2000	>	N	>	1000	rpm

The standard deviation using this correlation is 3.36 % and the goodness of fit is presented in CHAPTER VI.

Strictly speaking, above correlation is only valid when the reactor is operated at ambient temperatures and pressures. It can be used only for the purpose of estimating liquid holdup when such a parameter is needed.

CHAPTER VI

RESULTS AND DISCUSSION

Results of Visual Observation of Flow Uniformity of a Two Phase Mixture

From visual observations conducted at the room temperature, a total of four flow patterns with clear differences were observed.

Pattern 1

Liquid surface could be seen clearly and bubbles continuously emerged to the top surface of liquid and broke up there. Because of this bubbling, a small portion of the liquid randomly entered the catalyst basket from around the basket top perimeter as shown in Figure 3.

This flow pattern occurred when magnedrive speed was lower than 750 rpm. Changing the inlet liquid flow rate or the inlet gas flow rate did not change this flow pattern. An increase of pressure to 790 kPa (100 psig) did not change the flow pattern either.

Pattern 2

Liquid surface could not be seen clearly because of the turbulence of the bubble formation. The bubbles formed

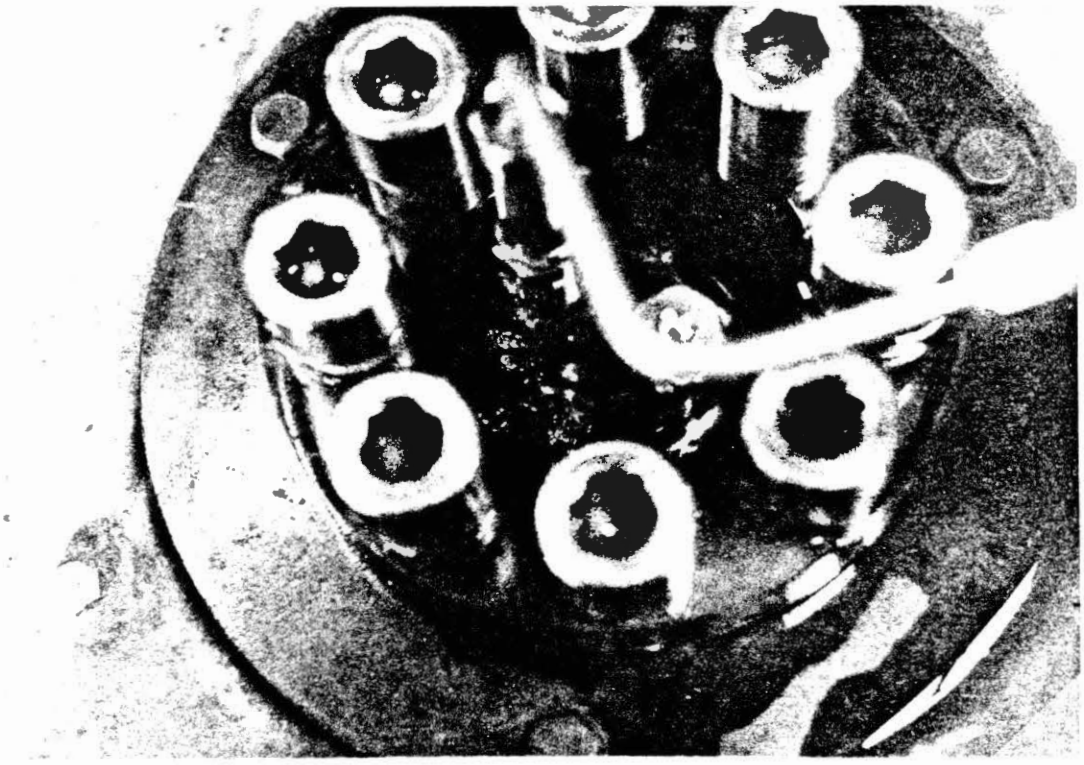

Figure 3. Liquid-Gas Mixture Flow Pattern at 500 rpm (Continuous Mode)

vigorously at the point where the gas inlet port was located. Periodically a bulk liquid moved upward from this point until it reached the reactor cap and then changed its direction downward entering the catalyst bed. Only a few bubbles could be seen in this liquid portion. See Figure 4 and Figure 5.

This flow pattern occurred when magnedrive speed was higher than 750 rpm and lower than 1750 rpm. Changing liquid flow rate did not produce any observable change in the flow pattern while a change in gas flow rate produce more bubbles. A pressure increase to 790 kPa (100) did not produce any appreciable change in the bubble size or flow pattern.

Pattern 3

The bulk liquid flow became almost consistent and a continuous circulation of liquid was formed. The path of liquid circulation was started from the point where the gas inlet port was located and moved upwards across the reactor cap then downwards to the catalyst basket. Few bubbles were entrained in this circulating liquid. No liquid surface could be observed. See Figure 6 and Figure 7.

This flow pattern occurred when magnedrive speed was higher than 1750 rpm. No appreciable changes were observed when liquid inlet flow rate, gas inlet flow rate and the reactor pressure were changed.

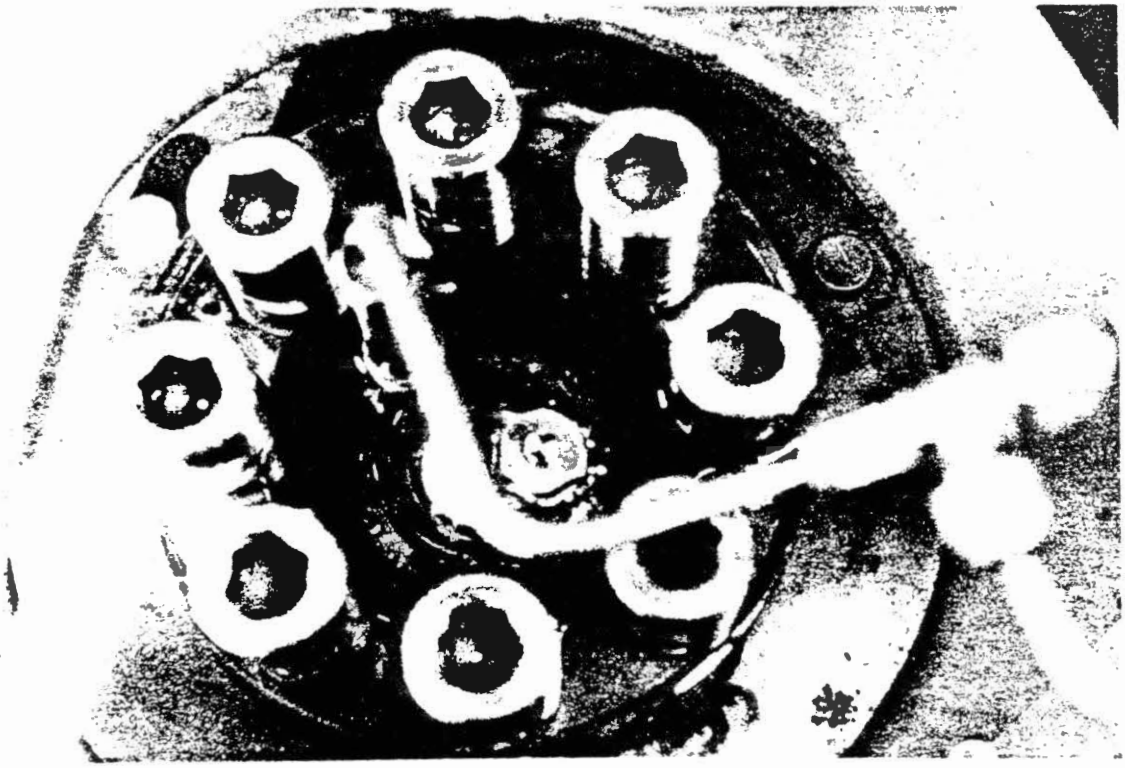

Figure 4. Liquid-Gas Mixture Flow Pattern at 1000 rpm (Continuous Mode)

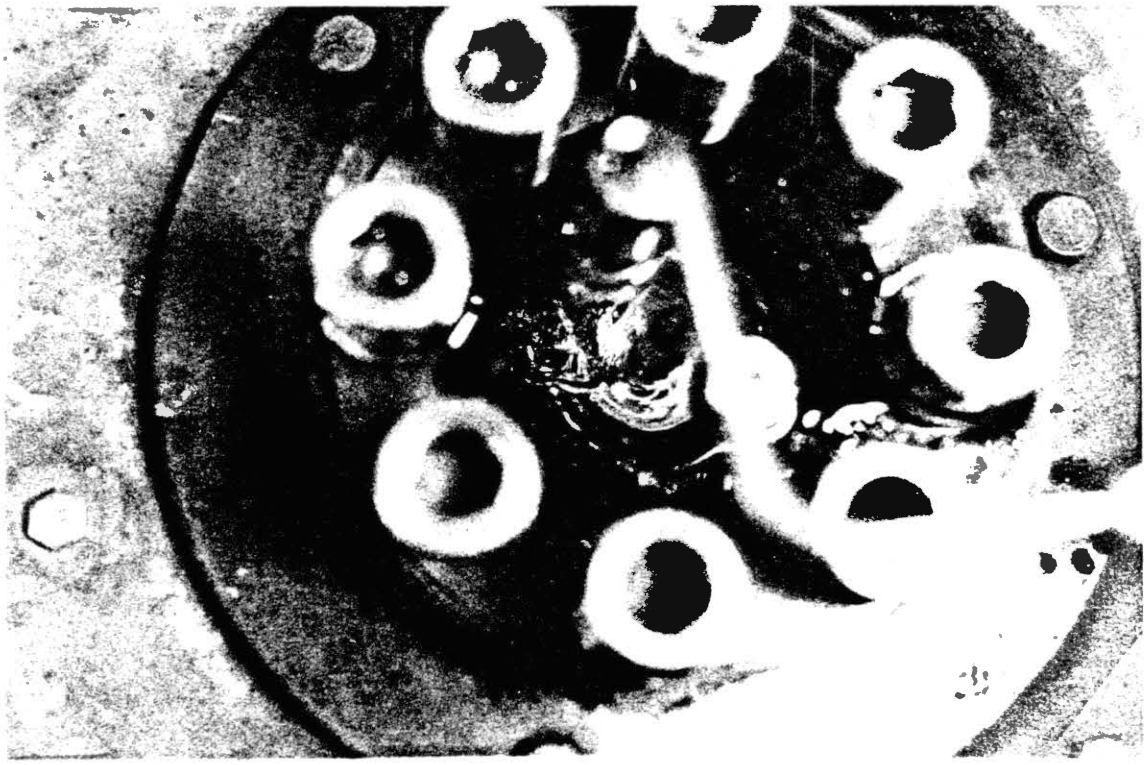

Figure 5. Liquid-Gas Mixture Flow Pattern at 1500 rpm (Continuous Mode)

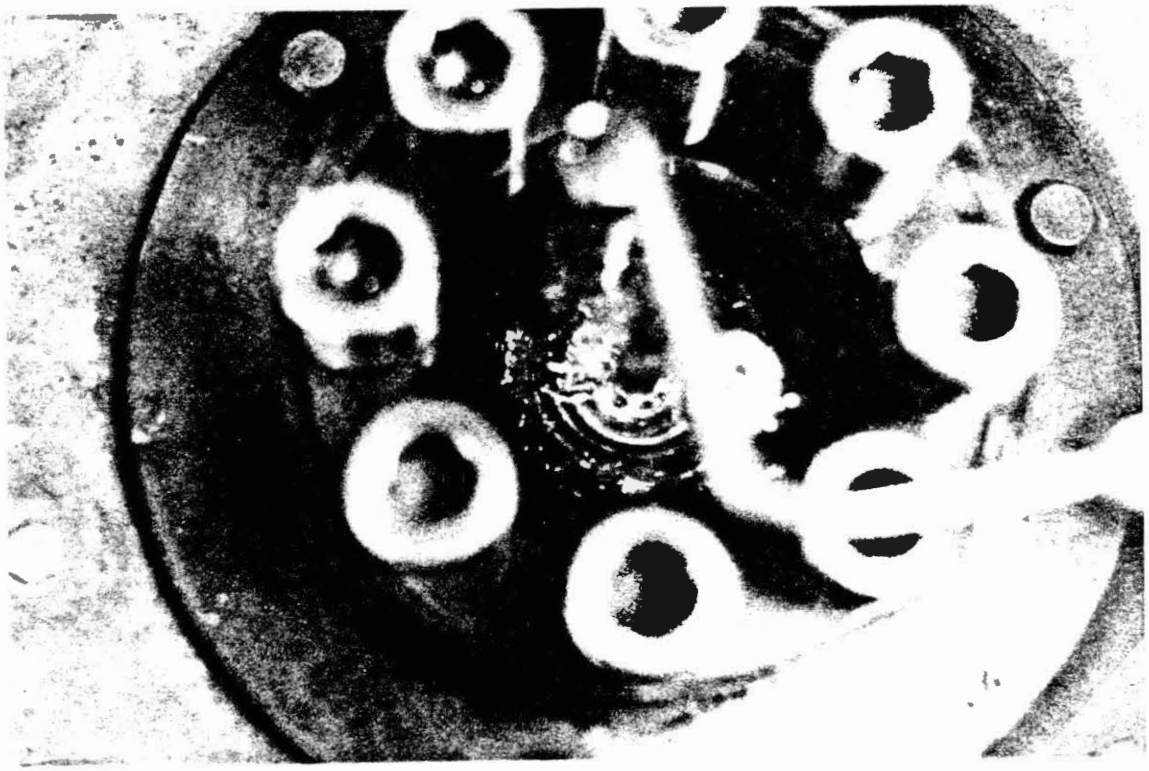

Figure 6. Liquid-Gas Mixture Flow Pattern at 2000 rpm (Continuous Mode)

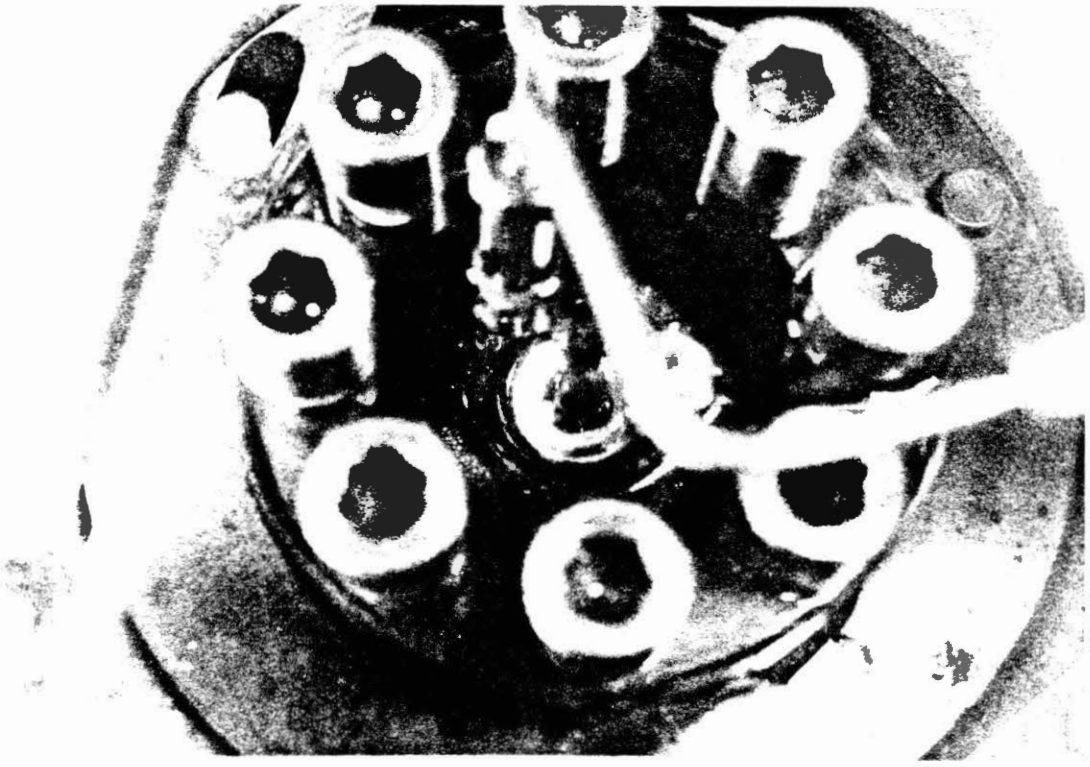

Figure 7. Liquid-Gas Mixture Flow Pattern at 2000 rpm (Continuous Mode)

Pattern 4

A froth or a bubbly liquid swarm was observed, where the bubble size was very uniform and was approximately 1 mm in diameter at 1000 rpm. See Figure 8.

This flow pattern occurred when the gas inlet line was turned off. Such a flow pattern did not exist when the magnedrive speed was less than 750 rpm. The bubble size continuously decreased when the magnedrive speed was increased and finally a very uniform gas-liquid mixture flow pattern was observed after 1500 rpm. Changes of inlet gas and liquid flow rate did not produce any visible change in the flow pattern. See Figure 9.

Results of the Liquid Holdup

Measurements of the Liquid Holdup

All liquid holdup measurements were conducted at room temperature while the pressure was varied from atmospheric condition to 5270 kPa (750 psig). The experimental data of the liquid holdup at hydrodynamic steady state along with operating conditions are given in Table III. Liquid Tetralin purchased from Aldrich Chemical Company was Used for most experimental runs and nitrogen was used for the low temperature and low pressure runs while hydrogen was used for high pressure runs. The total liquid entrained with exiting gas was very small and was about 5 ml when the steady state

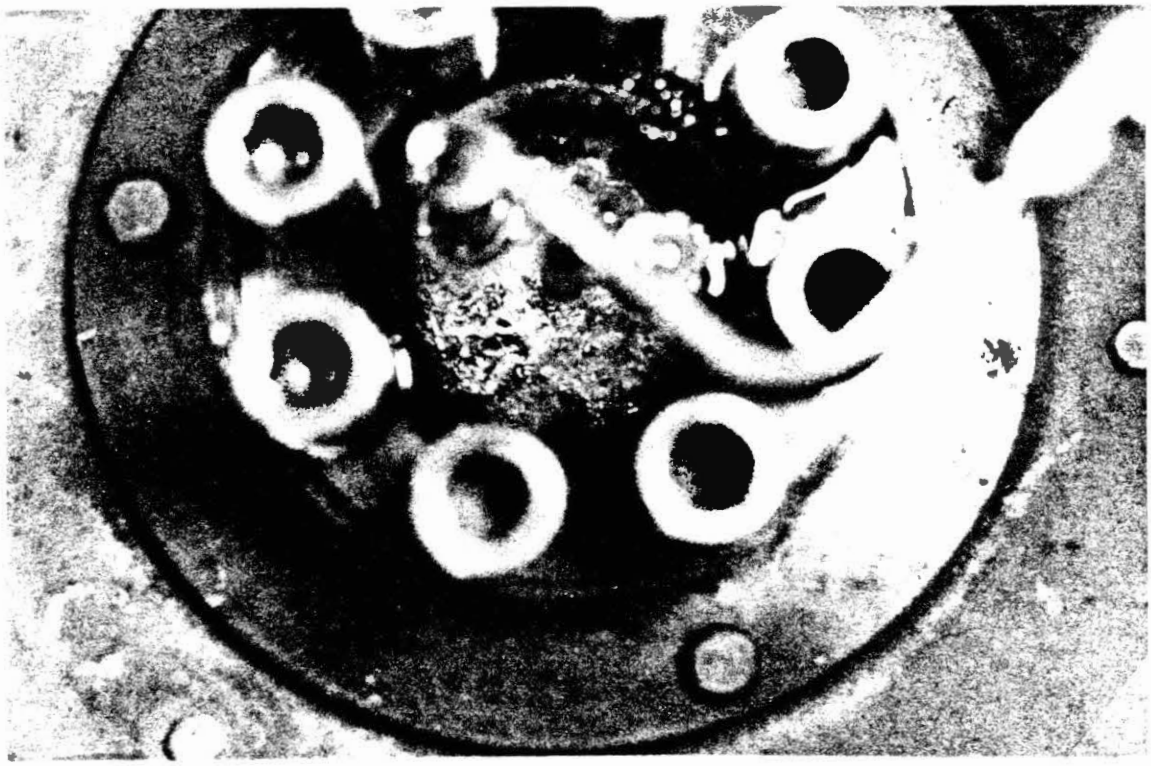

Figure 8. Liquid-Gas Mixture Flow Pattern at 1000 rpm (Batch Mode)

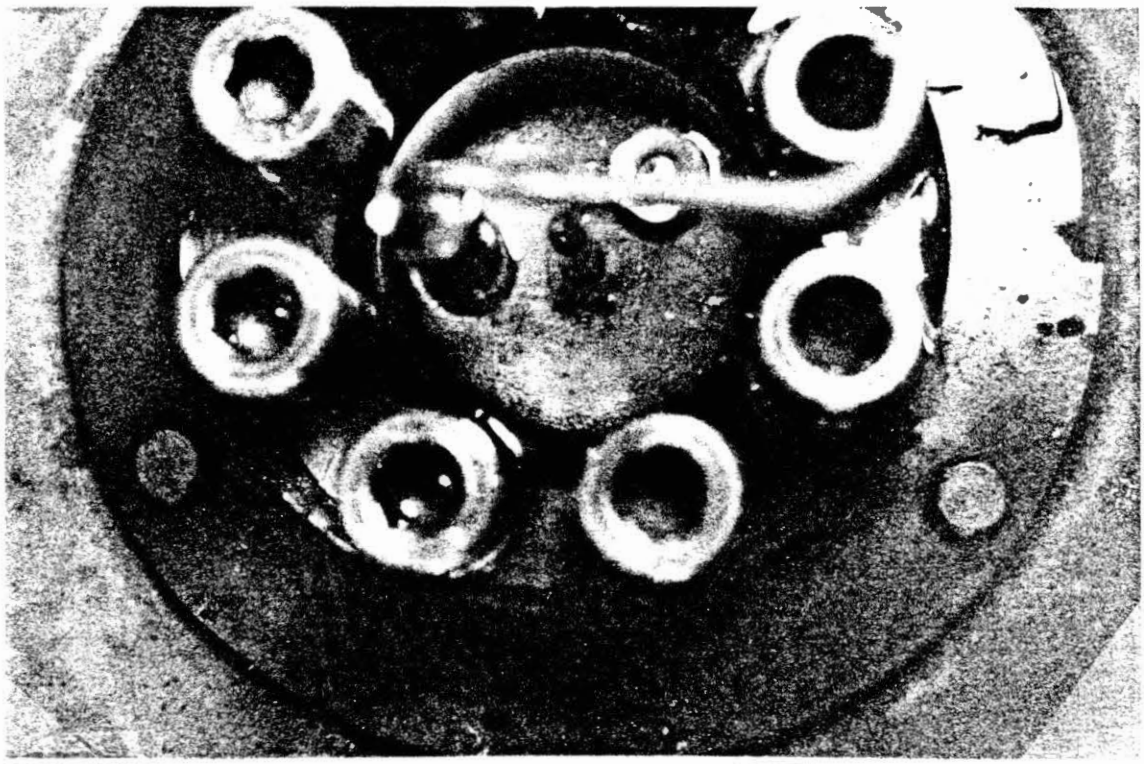

Figure 9. Liquid-Gas Mixture Flow Pattern at 2000 rpm (Batch Mode)

TABLE III

HYDRODYNAMIC STEADY STATE LIQUID HOLDUP

	Temperature °C	Pressure psig	Magnedrive Speed rpm	Liquid In ml/min	Gas In ml/min	Liquid Holdup Average ml
	20	100	1500	4.7	750	105 ± 1.5
	20	100	2000	4.7	750	108 ± 1.7
	20	100	1500	2.5	750	96 ± 3.2
	20	100	1500	5.0	1125	96 ± 2.3
	20	100	1500	2.5	1125	100 ± 2.7
	20	750	1500	4.7	750	102 ± 1.4
*	20	100	1500	4.8	750	103
*	20	100	1500	4.8	1125	98
	20	100	1500	2.5	0	170 ± 12.0
	35	0	500	3.6	1250	140 ± 5.8
	35	0	1000	3.6	1250	119 ± 7.3
	35	0	1500	3.6	1250	100 ± 3.5
	35	0	2000	3.6	1250	93 ± 4.6
	35	0	500	3.6	250	227 ± 21.0
	35	0	1000	3.6	250	153 ± 16.0
	35	0	1500	3.6	250	139 ± 18.0
	35	0	2000	3.6	250	113 ± 3.6

* Water is used and no repeated run.

was reached. Since the experimental error was about 5 ml, the liquid entrainment was not further measured. For two experimental runs, water was used as liquid in order to test the effect of changing the physical properties on the liquid holdup at steady state.

Estimation of Liquid Holdup

Unsteady state liquid holdup estimated using Eq. V-15 for a given set of experimental conditions is shown on Figure 10 together with the experimental measurements at ambient temperature and pressure. Figure 11 shows calculation results of the steady state liquid holdup at two elevated temperature and pressure conditions for the hydrogen / Tetralin binary. The goodness of correlation (Eq. V-23) for estimating steady state liquid holdup at ambient condition is shown on Figure 12. The standard deviation using this correlation is 3.36 %.

Results of Phase Equilibrium Calculation

Interaction Parameters fitted from the ten binary (See Table II) experimental data are given in Table IV and Table V. Figure 13 and Figure 14 shown the plots of C_{ij} and D_{ij} over the temperature for the hydrogen / Tetralin mixture as a typical binary system. Table VI gives average absolute deviation in K-values for ten binary system, which actually gives the indication of goodness of the binary data fitting.

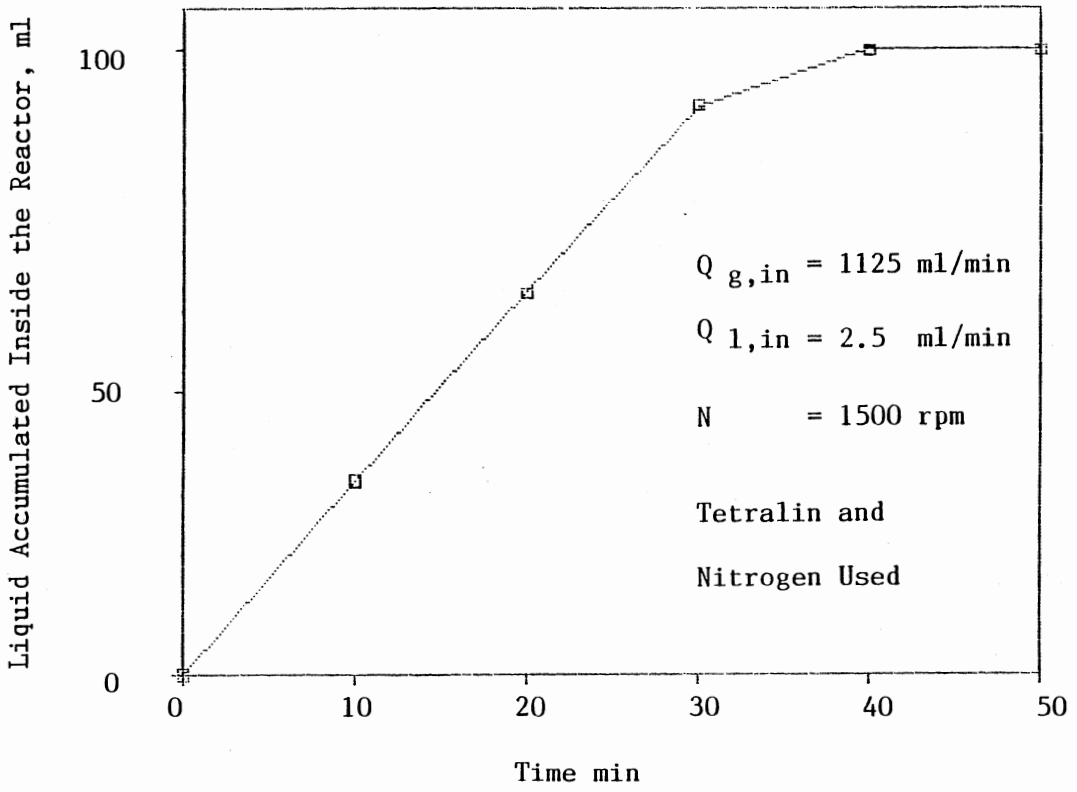

Figure 10. Observed Liquid Accumulation Process

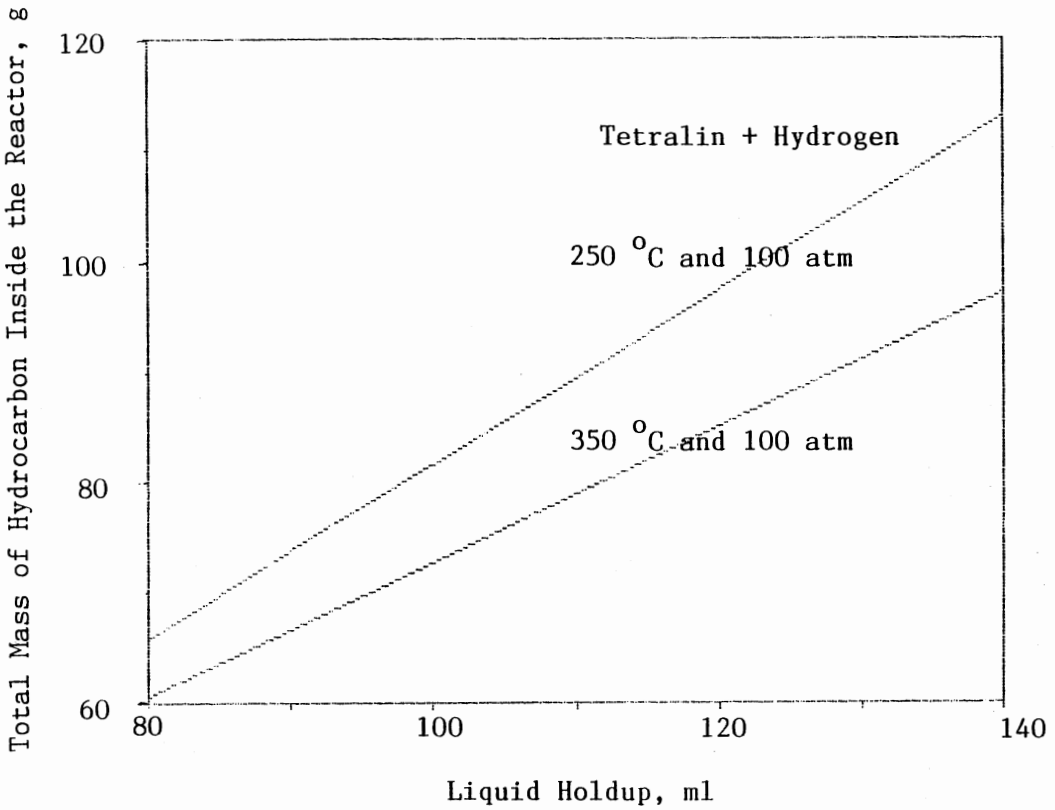

Figure 11. Relation Between Steady State Liquid Holdup and Total Hydrocarbon Mass Inside the Reactor at High Temperatures and Pressures

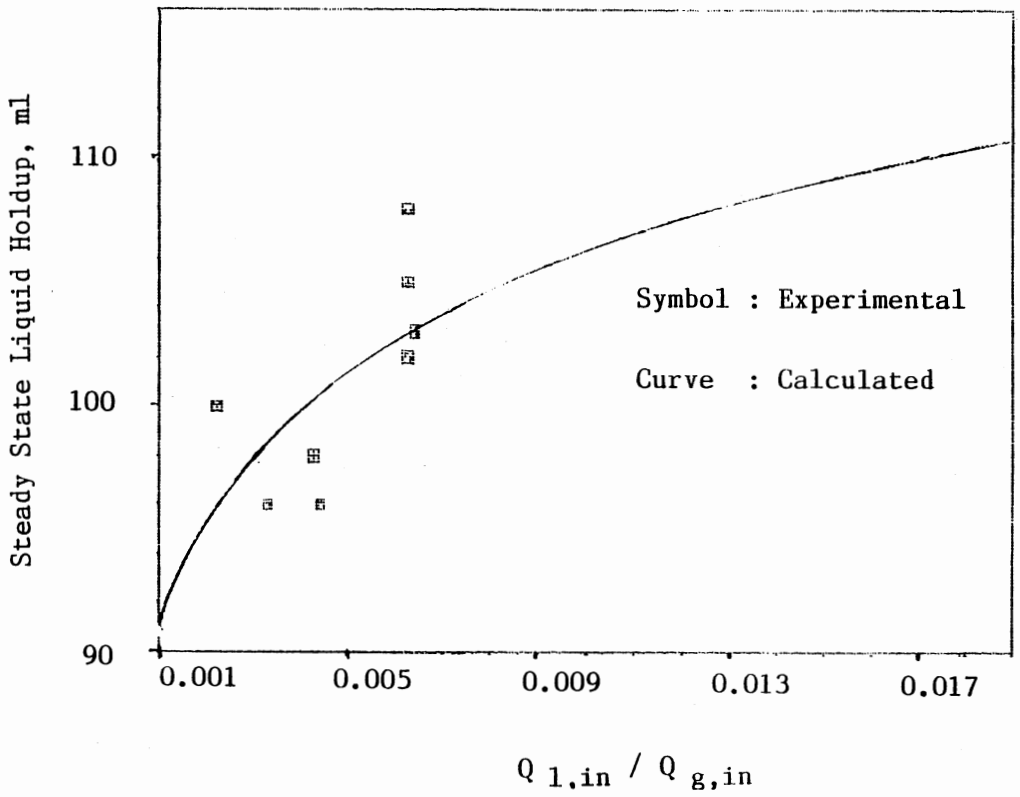

Figure 12. Comparison of the Experimental and Calculated Steady State Liquid Holdup at 20 ^{o}C

TABLE IV

INTERACTION PARAMETER C ij (D ij = 0)

Hydrogen / Tetralin

Pressure atm	Temperature °C 189	269	349	389
20	0.25	0.27	-	-
30	0.25	0.36	-	-
50	0.17	0.39	0.52	0.11
100	0.10	0.36	0.61	0.25
150	0.12	0.33	0.52	0.24
200	0.13	0.23	0.34	0.16
250	0.13	0.20	0.27	0.09

Hydrogen / 9,10-Dihydrophenanthrene

Pressure atm	Tempreature °C 188	269	350	430
20	0.39	0.59	-	-
30	0.44	0.55	-	-
50	0.48	0.53	-	-
100	0.55	0.50	-	-
150	0.44	0.49	-	-
200	0.52	0.34	-	-
250	0.35	0.29	-	-

Hydrogen / n-Hexadecane

Pressure atm	Temperature °C 189	269	350	391
20	-0.12	-0.14	-0.06	-0.09
30	-0.06	-0.13	-0.01	-0.05
50	-0.04	-0.05	0.04	0.01
100	-0.06	0.16	0.19	0.03
150	0.13	0.15	0.18	0.15
200	0.18	0.14	0.12	0.10
250	0.20	0.14	0.19	0.09

TABLE IV (Continued)

Hydrogen / m-Xylene

Pressure atm	Temperature ° C 189	229	269	309
20	0.44	0.64	0.52	-
30	0.42	0.49	0.48	0.41
50	0.39	0.50	0.50	0.23
100	0.32	0.47	0.31	0.13
150	0.19	0.24	0.31	0.09
200	0.13	0.25	0.18	0.09
250	0.05	0.20	0.12	0.04

Hydrogen / 1-Methynaphthalene

Pressure atm	Temperature ° C 189	269	349	429
20	0.19	0.31	0.29	-
30	0.20	0.23	0.37	0.07
50	0.20	0.20	0.38	0.09
100	0.19	0.25	0.37	0.17
150	0.20	0.21	0.30	0.05
200	0.19	0.19	0.21	-0.03
250	0.19	0.16	0.10	-0.09

Hydrogen / Cyclohexane

Pressure atm	Temperature ° C 71	104	138
68	0.41	0.42	0.40
137	0.25	0.28	0.31
205	0.15	0.17	0.22
274	0.08	0.11	0.17
342	0.03	0.07	0.13
411	0.01	0.05	0.12
479	-	0.03	0.07
548	-0.01	0.02	0.06

TABLE IV (Continued)

Hydrogen / m-Cresol

Pressure atm	Temperature °C 189	230	269	309	348	389
20	0.28	0.34	0.47	0.59	0.64	-
30	0.24	0.33	0.40	0.50	0.47	0.25
0.26	0.39	0.42	0.50	0.45	0.18	
100	0.26	0.40	0.37	0.48	0.32	0.14
150	0.26	0.35	0.33	0.40	0.27	0.10
200	0.25	0.32	0.29	0.35	0.21	0.02
250	0.22	0.25	0.30	0.31	0.23	0.05

50

Hydrogen / n-Decane

Pressure atm	Temperature °C 189	230	270	310
20	0.35	0.26	0.45	-
30	0.20	0.33	0.43	-
50	0.30	0.35	0.36	0.38
100	0.35	0.31	0.37	0.29
150	0.26	0.28	0.32	0.14
200	0.20	0.24	0.29	0.06
250	0.22	0.20	0.23	-0.08

Hydrogen / Diphenylmethane

Pressure atm	Temperature °C 189	269	349	429
20	0.30	0.48	0.62	-30
0.28	0.43	0.62	0.38	
50	0.29	0.39	0.58	0.54
100	0.24	0.36	0.59	0.34
150	0.29	0.32	0.42	0.27
200	0.27	0.26	0.30	0.31
250	0.26	0.19	0.29	0.28

TABLE IV (Continue)

Hydrogen / Toluene

Pressure atm	Temperature ^{o} C 189	229	269	302
20	0.41	0.53	-	-
30	0.44	0.49	0.44	-
50	0.34	0.40	0.42	0.34
100	0.24	0.36	0.35	0.34
150	0.18	0.28	0.09	0.00
200	0.07	0.13	0.01	-0.09
250	-0.02	0.02	0.00	-0.26

TABLE V

INTERACTION PARAMETER D ij (C ij = 0)

Hydrogen / Tetralin

Pressure atm	Temperature °C 189	269	349	389
20	0.021	0.025	-	-
30	0.022	0.034	-	-
50	0.019	0.039	0.059	0.017
100	0.020	0.043	0.085	0.050
150	0.022	0.048	0.087	0.065
200	0.024	0.044	0.071	0.064
250	0.023	0.047	0.067	0.057

Hydrogen / 9,10-Dihydrophenanthrene

Pressure atm	Temperature °C 188	269	350	430
20	0.024	0.038	-0.005	-0.011
30	0.027	0.039	-0.002	-0.002
50	0.026	0.038	-0.003	0.003
100	0.028	0.041	-0.007	0.008
150	0.029	0.041	0.018	0.033
200	0.033	0.037	0.021	0.038
250	0.030	0.038	0.050	0.052

Hydrogen / n-Hexadecane

Pressure atm	Temperature °C 189	269	350	391
20	-0.010	-0.012	-0.005	-0.011
30	-0.013	-0.012	-0.002	-0.002
50	-0.012	-0.013	-0.003	0.003
100	-0.010	0.007	-0.007	0.008
150	-0.008	0.003	0.018	0.033
200	0.001	0.001	0.021	0.038
250	0.005	0.009	0.050	0.052

TABLE V (Continued)

Hydrogen / m-Xylene

Pressure atm	Temperature ° C 189	229	269	309
20	0.047	0.073	0.062	-
30	0.045	0.058	0.061	0.055
50	0.045	0.062	0.068	0.037
100	0.045	0.065	0.060	0.044
150	0.040	0.050	0.072	0.051
200	0.038	0.057	0.063	0.067
250	0.033	0.054	0.059	0.048

Hydrogen / 1-Methylnathalene

Pressure atm	Temperature ° C 189	269	349	429
20	0.014	0.026	0.027	-
30	0.015	0.020	0.036	0.010
50	0.017	0.019	0.040	0.015
100	0.018	0.028	0.049	0.046
150	0.020	0.029	0.053	0.045
200	0.022	0.031	0.046	0.043
250	0.024	0.030	0.039	-0.046

Hydrogen / Cyclohexane

Pressure atm	Temperature ° C 71	104	138
68	0.056	0.059	0.060
137	0.046	0.054	0.061
205	0.041	0.048	0.059
274	0.036	0.045	0.060
342	0.030	0.041	0.059
411	0.026	0.037	0.069
479	-	0.031	0.050
548	0.017	0.027	0.046

TABLE V (Continued)

Hydrogen / m-Cresol

Pressure atm	Temperature °C 189	230	269	309	348	389
20	0.025	0.031	0.046	0.062	0.070	-
30	0.021	0.031	0.040	0.053	0.054	0.029
50	0.024	0.036	0.043	0.053	0.056	0.025
100	0.023	0.038	0.043	0.060	0.051	0.035
150	0.023	0.037	0.040	0.058	0.055	0.042
200	0.025	0.038	0.042	0.058	0.053	0.033
250	0.022	0.028	0.044	0.057	0.063	0.047

Hydrogen / n-Decane

Pressure atm	Temperature °C 189	230	270	310
20	0.028	0.023	0.044	-
30	0.016	0.029	0.042	-
50	0.022	0.030	0.037	0.056
100	0.026	0.031	0.051	0.068
150	0.023	0.036	0.058	0.059
200	0.025	0.046	0.072	0.056
250	0.036	0.042	0.082	-0.007

Hydrogen / Diphenylmethane

Pressure atm	Temperature °C 189	269	349	429
20	0.023	0.036	0.050	-
30	0.023	0.033	0.052	0.037
50	0.024	0.032	0.054	0.061
100	0.022	0.034	0.069	0.064
150	0.027	0.040	0.065	0.071
200	0.030	0.041	0.062	0.089
250	0.034	0.038	0.064	0.100

TABLE V (Continued)

Hydrogen / Toluene

Pressure atm	Temperature °C 189	229	269	302
20	0.051	0.068	-	-
30	0.055	0.066	0.062	-
50	0.047	0.059	0.067	0.092
100	0.048	0.067	0.058	0.092
150	0.051	0.068	0.052	0.022
200	0.048	0.055	0.040	-0.040
250	0.041	0.046	0.170	-0.065

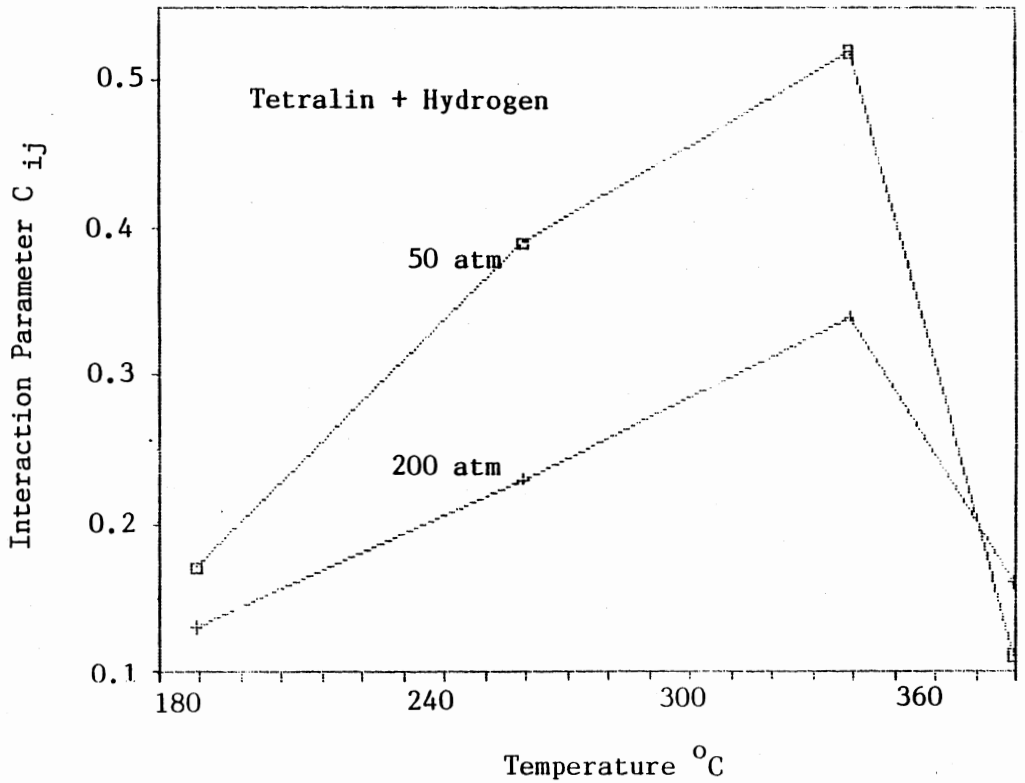

Figure 13. Temperature Dependence of C_{ij} ($D_{ij} = 0$)

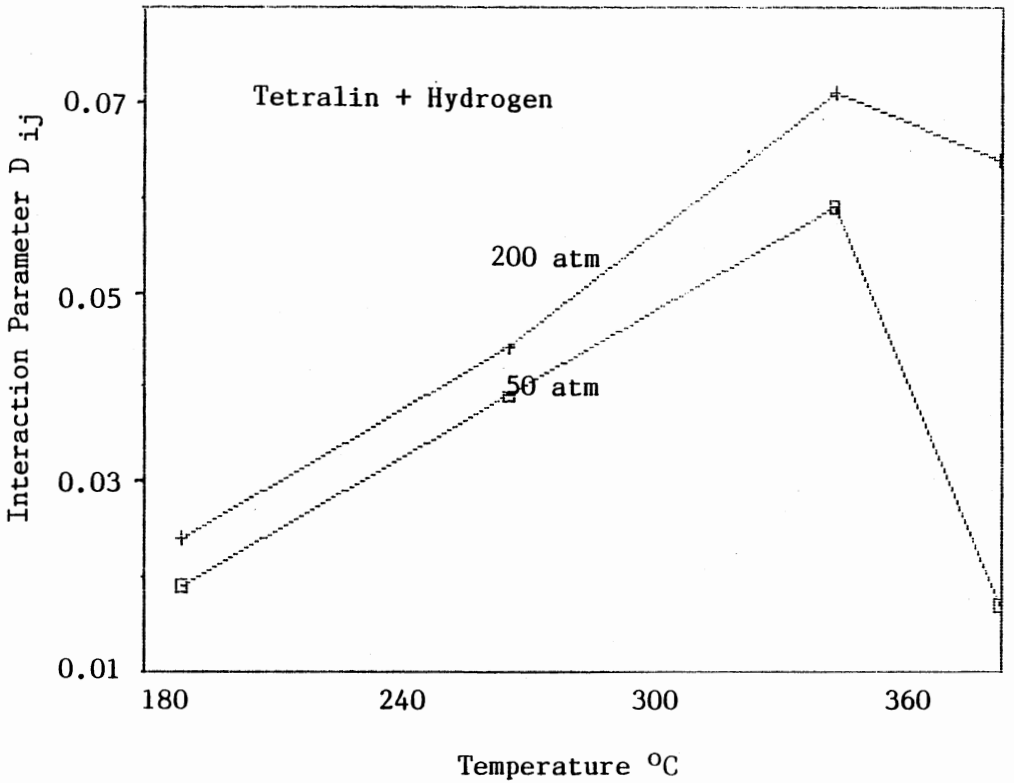

Figure 14. Temperature Dependence of D_{ij} ($C_{ij} = 0$)

TABLE VI

GOODNESS OF THE BINARY DATA FITTING

System ID Number	Data Points Used	At C ij ≠ 0 and D ij = 0	
		AADK $_{HC}$	AADK $_{H2}$
1	24	5.4	3.4
2	14	4.6	3.4
3	28	4.5	4.5
4	27	4.3	3.0
5	27	6.4	3.2
6	37	5.4	8.5
7	41	3.3	1.6
8	26	3.2	2.0
9	27	6.0	3.5
10	25	5.9	3.7

GOODNESS OF THE BINARY DATA FITTING

System ID Number	Data Points Used	At C ij = 0 and D ij ≠ 0	
		AADK $_{HC}$	AADK $_{H2}$
1	24	2.9	0.3
2	14	16.4	1.8
3	28	9.1	2.0
4	27	3.3	1.1
5	27	5.2	0.4
6	37	3.6	0.9
7	41	5.3	0.4
8	26	9.9	2.0
9	27	5.3	0.9
10	25	5.9	1.2

Table VII and Table VIII give the calculation results for two ternary system by direct use of interaction parameters fitted from corresponding binaries. Typical isothermal flash calculation results are given in Table IX for hydrogen / Tetralin / cis-decalin / trans-decalin quartery system by using those interaction parameters listed in Table IV (In the calculation, D_{ij} is kept as zero. The C_{ij} of hydrogen / Tetralin binary was used for that of hydrogen cis-decalin and hydrogen / trans-decalin because of the lack of the experimental data for this two binary systems and similar molecular structure between decalin and Tetralin).

Results of the Reactor Start-up Modeling

Figure 15 presents plots of Y_{H2} over the dimensionless time t^* at three different level of R_m, the molar feed ratio of hydrocarbon to hydrogen. The initial hydrogen mole fraction in the vapor phase is taken as 1.0 in making these plots, which in turn implies that the reactor is started up in the pure hydrogen atmosphere. Figure 16 shows the hydrogen mole fraction at infinite time at different R_m values. This figure actually defines the phase boundary inside the reactor as discussed later. Figure 17 emphasizes the different time requirements for the initially "dry and hot" reactor to reach its dew point at different R_m.

The study of flow uniformity of a vapor-liquid two phase mixture inside the Berty reactor indicated that the flow

TABLE VII

VAPOR - LIQUID EQUILIBRIUM CALCULATION FOR TERNARY SYSTEM
$C_{ij} \neq 0$ and $D_{ij} = 0$

Hydrogen / Tetralin / Diphenylmethane

Temperature	Pressure	Interaction		Absolute Average Deviation		
^{o}C	Range (atm)	C_{HT}	C_{HD}	$AADK_{H2}$	$AADK_{T}$	$AADK_{D}$
188	20 - 250	0.24	0.24	4.8	6.6	10.6
268	20 - 250	0.39	0.45	3.9	3.7	4.3
348	30 - 250	0.53	0.62	5.8	5.0	5.9
428	30 - 250	0.34	0.51	3.7	1.5	3.6
			Average	4.5	3.9	5.7

Hydrogen / Tetralin / m-Xylene

Temperature	Pressure	Interaction		Absolute Average Deviation		
^{o}C	Range (atm)	C_{HT}	C_{HM}	$AADK_{H2}$	$AADK_{T}$	$AADK_{M}$
189	20 - 250	0.24	0.35	3.5	2.1	15.8
229	20 - 250	0.32	0.47	3.3	3.6	11.1
270	20 - 250	0.39	0.41	2.3	4.8	5.0
309	20 - 250	0.46	0.26	1.3	5.2	3.6
			Average	2.6	3.9	8.9

Data Source : (39)
AADK is the average absolute percentage deviation of K-value.
Subscripts H2, T, D, M refer to the corresponding components.
C is the interaction parameter.
Subscripts HT, HD, HM refer to the interaction between hydrogen and Tetralin, diphenylmethane, m-xylene.

TABLE VIII

VAPOR - LIQUID EQUILIBRIUM CALCULATION FOR TERNARY SYSTEM
$C_{ij} = 0$ and $D_{ij} \neq 0$

Hydrogen / Tetralin / Diphenylmethane

Temperature	Pressure	Interaction		Absolute Average Deviation		
°C	Range (atm)	D_{HT}	D_{HD}	$AADK_{H2}$	$AADK_{T}$	$AADK_{D}$
188	20 - 250	0.021	0.024	2.1	11.7	13.7
268	20 - 250	0.040	0.035	3.0	5.6	11.1
348	30 - 250	0.072	0.060	4.1	6.1	7.1
428	30 - 250	0.054	0.068	2.7	0.86	0.9
		Average		3.0	5.4	7.4

Hydrogen / Tetralin / m-Xylene

Temperature	Pressure	Interaction		Absolute Average Deviation		
°C	Range (atm)	D_{HT}	D_{HM}	$AADK_{H2}$	$AADK_{T}$	$AADK_{M}$
189	20 - 250	0.021	0.042	4.2	7.9	10.6
229	20 - 250	0.031	0.056	3.2	3.4	5.4
270	20 - 250	0.036	0.063	3.0	2.6	2.0
309	20 - 250	0.056	0.054	1.5	1.4	2.3
		Average		3.0	3.8	5.1

Data Source : (39)
AADK is the average absolute percentage deviation of K-value.
Subscripts H2, T, D, M refer to the corresponding components.
D is the interaction parameter.
Subscript HT, HD, HM refer to the interaction between hydrogen and Tetralin, diphenylmethane, m-xylene.

TABLE IX

SOME TYPICAL ISOTHERMAL FLASH CALCULATION RESULTS OF HYDROGEN/TETRALIN/CIS-DECALIN/TRANS-DECALIN SYSTEM AT 350 ^{o} C AND 100 atm

V/F = .1194	Hydrogen	Tetralin	cis-Decalin	trans-Decalin
Feed	0.2	0.3	0.2	0.3
Vaopr	0.8232	0.0632	0.0452	0.0685
Liquid	0.1157	0.3320	0.2209	0.3313
K-value	7.0960	0.1898	0.2039	0.2060
V/F = .2622	Hydrogen	Tetralin	cis-Decalin	trans-Decalin
Feed	0.3	0.3	0.2	0.2
Vapor	0.8254	0.0717	0.0512	0.0517
Liquid	0.1136	0.3810	0.2528	0.2526
K-value	7.2577	0.1877	0.2022	0.2044
V/F = .4039	Hydrogen	Tetralin	cis-Decalin	trans-Decalin
Feed	0.4	0.3	0.2	0.1
Vapor	0.8280	0.0829	0.0592	0.0299
Liquid	0.1105	0.4469	0.2953	0.1474
K-value	7.4851	0.1851	0.2001	0.2026
V/F = .6807	Hydrogen	Tetralin	cis-Decalin	trans-Decalin
Feed	0.6	0.2	0.1	0.1
Vapor	0.8288	0.0831	0.0439	0.0442
Liquid	0.1117	0.4495	0.2198	0.2190
K-value	7.4310	0.1851	0.1999	0.2023
V/F = .8246	Hydrogen	Tetralin	cis-Decalin	trans-Decalin
Feed	0.7	0.1	0.1	0.1
Vapor	0.8240	0.0571	0.0593	0.0596
Liquid	0.1168	0.3016	0.2915	0.2901
K-value	7.0611	0.1896	0.2036	0.2056
V/F = .9587	Hydrogen	Tetralin	cis-Decalin	trans-Decalin
Feed	0.8	0.1	0.05	0.05
Vapor	0.8296	0.0846	0.0429	0.0430
Liquid	0.1116	0.4593	0.2156	0.2135
K-value	7.4543	0.1846	0.1994	0.2018

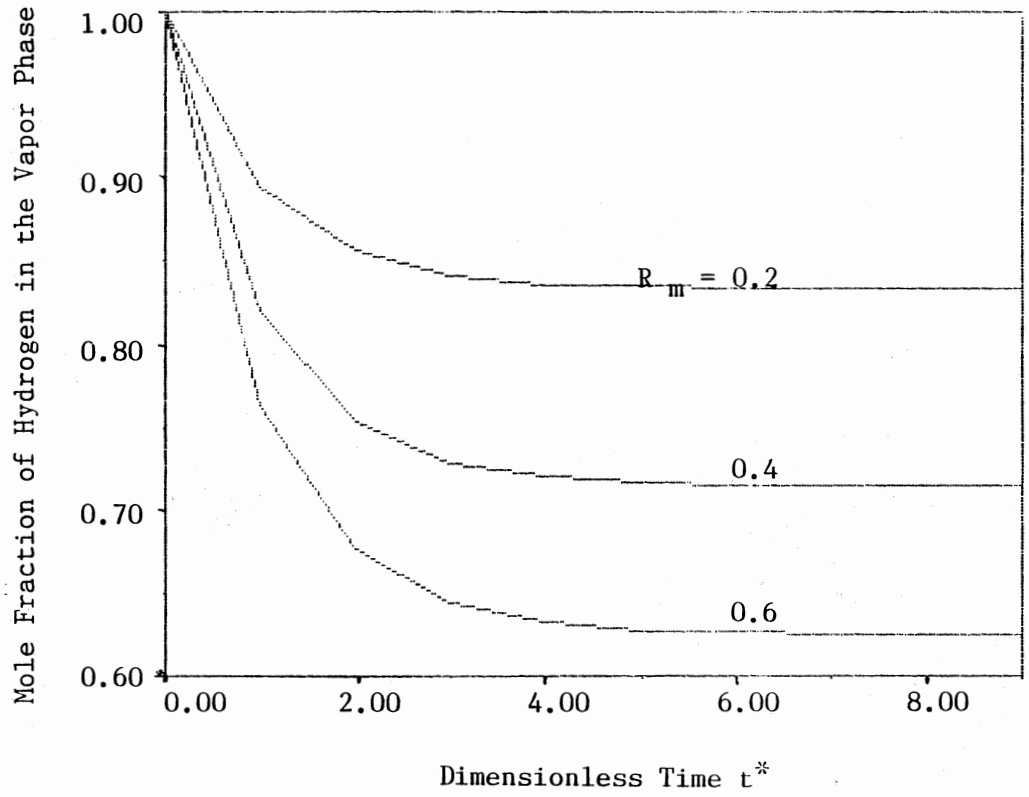

Figure 15. Transient Behavier of Hydrogen Mole Fraction During the Reactor Start-up Process

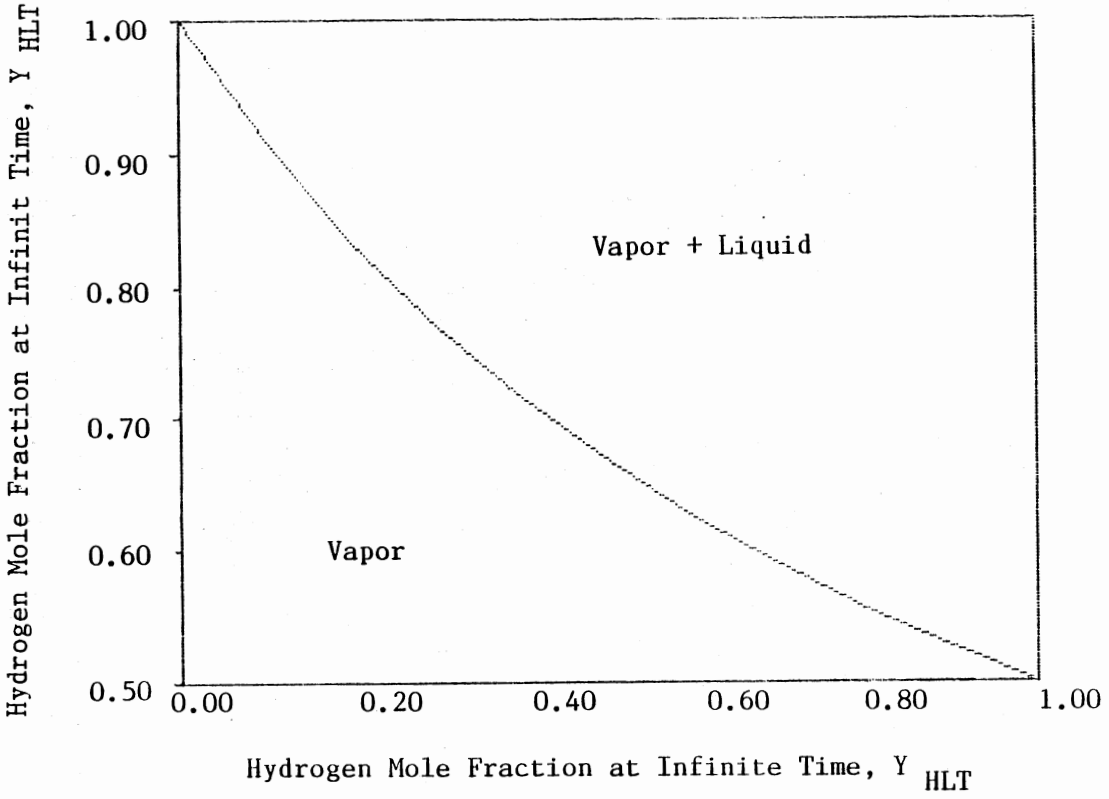

Figure 16. Map of the Reactor Operation Region

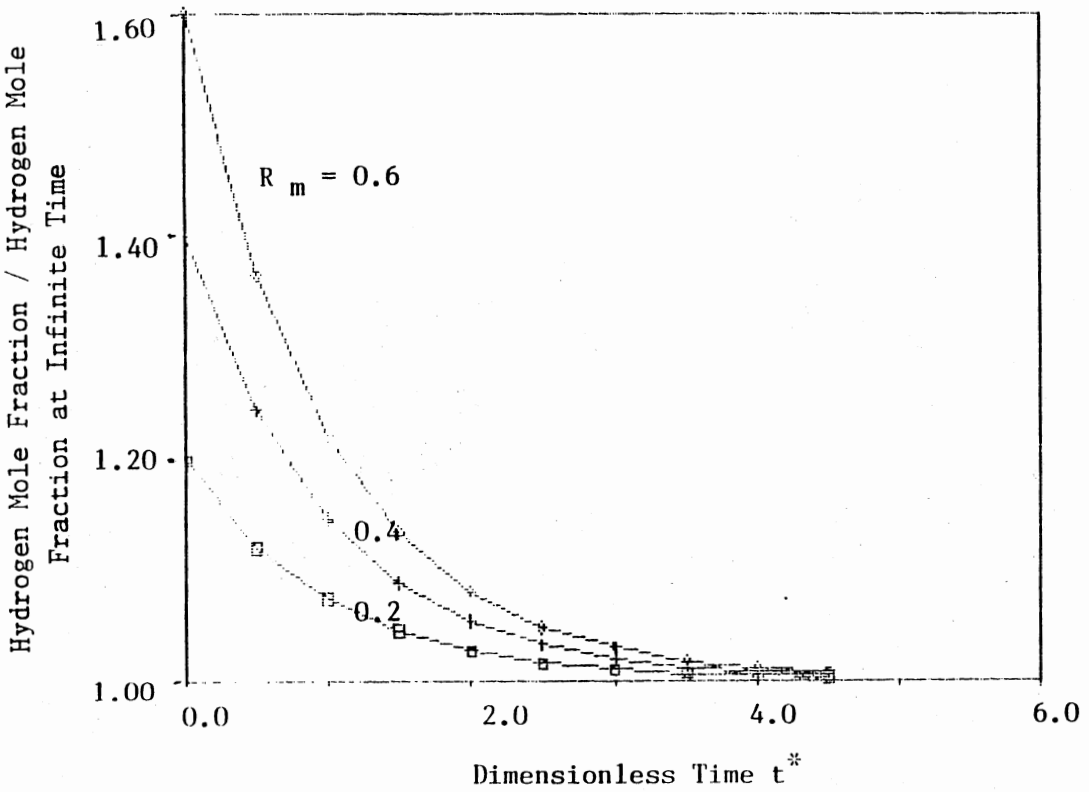

Figure 17. Variation of Hydrogen Mole Fraction Ratio With Time During the Reactor Start-up Process

pattern would be affected by the magnedrive speed and the operation mode. Liquid holdup measurements indicated that steady state liquid would gradually approach a fixed value when magnedrive speed exceeds 1500 rpm. Modeling the phase behavior of the heavy hydrocarbon-hydrogen system indicated that the magnedrive speed, molar feed ratio of hydrocarbon to hydrogen and phase equilibria would influence the phase transition process inside the reactor. In addition, liquid accumulation process was affected by several parameters. Following is a discussion of the effects of different parameters on the results obtained in this work.

Discussion on the Visual Observation of the Flow Uniformity of a Two Phase Mixture

From the visual observations at ambient temperature and pressure, the magnedrive speed had shown to have a major effect on flow patterns of a two phase mixture, as described in CHAPTER III. However, no matter what the magnedrive speed was, a completely uniform flow pattern was never observed when the reactor was operated in a continuous mode (continuous mode refers to that reactor was operated as a continuous flow reactor while batch mode refers to that reactor was operated as a batch reactor). This might be also true when the reactor was operated at high temperatures and pressures. As a supporting evidence, Tscheikuna (5) found that there was a maximum conversion of Tetralin around 1500

rpm when the magnedrive speed was continuously increased from 1000 to 2000 rpm. Another supporting evidence was that coke had a non-uniform distribution in the catalyst bed (5).

Effect of The Operation Mode

When the reactor was operated in a batch mode, a uniform flow pattern of two phase mixture was observed. This suggested that the Berty reactor might generate better kinetic results when it was operated in a batch mode than in continuous flow mode.

Discussion on the Liquid Holdup Study

Effect of Liquid Entrainment on Unsteady State Liquid Holdup

The total liquid entrainment due to the exiting gas was found about 5 ml in this work. Since the experimental error was also about 5 ml, the liquid entrainment could be neglected at low temperature and pressure conditions. At high temperatures and pressures, however, the liquid entrainment might increase. This would result in that the rate of the increase of the liquid holdup become lower than the one given by Eq. V-15. Thus the time needed for the reactor to reach its hydrodynamic steady state would become longer.

Effect of Phase Equilibrium on Unsteady State Liquid Holdup

The phase equilibrium has an important effect on the liquid accumulation process. Temperature, pressure and inlet flow rate of each component determine the Q_{LIN} and thus determine the level of the liquid holdup at any time during the liquid accumulation process.

Effect of Magnedrive Speed on
Steady State Liquid Holdup

From Table III, it is obvious that an increase of magnedrive speed will result in a decrease of steady state liquid holdup when the magnedrive speed is lower than 1500 rpm. When magnedrive speed is higher than 1500 rpm, however, further increase of the magnedrive speed does not produce any appreciable change of liquid holdup.

Effect of Volumetric Feeds Ratio
on Steady State Liquid Holdup

From the correlation developed in CHAPTER V (See Eq. V-19), it is obvious that the higher the ratio of liquid volumetric feed rate to gas volumetric feed rate, the higher liquid holdup will be at steady state. This also can be seen in Figure 18 which is a plot of experimental results of the steady state liquid holdup.

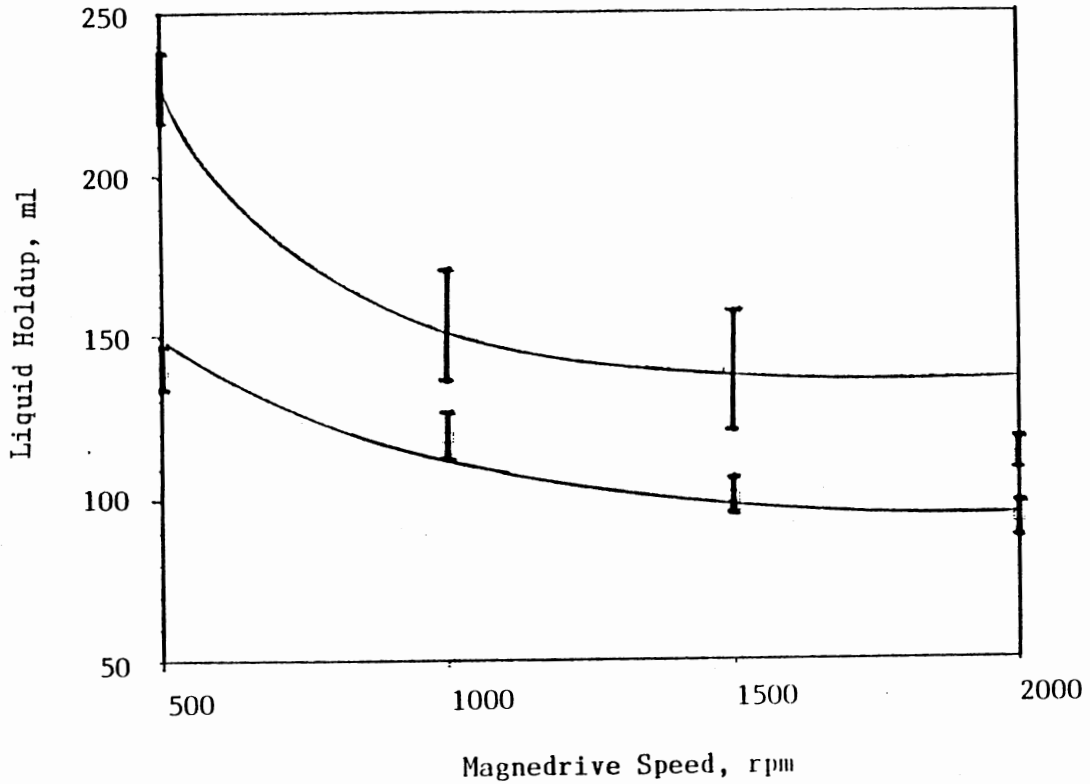

Figure 18. Variation of the Steady State Liquid Holdup With the Magnedrive Speed

Effect of Physical Property

When water is used instead of Tetralin, it is found that the liquid holdups differ slightly from those obtained using Tetralin at the same operating conditions. Since water is a completely different material comparing with the liquid Tetralin, it seems that the steady state liquid holdup is not greatly affected by the change in the physical property. This in turn indicates that the steady state liquid holdup may be regarded as a reactor structure related parameter when magnedrive speed is higher than 1500 rpm.

Experimental Error and Goodness of Fit of Steady State Liquid Holdup

The experimental error in the measurement of the steady state is given in Table III. The causes of the error may attribute to the random existence of liquid droplets left in the tubing and on the inner walls of the separation cylinder. The loss of liquid droplet to the purge gas may also had some contribution to the experimental error. Such experimental error may lead to an over or under estimate the time requirement for the reactor to reach its hydrodynamic steady state.

From Figure 12, it is apparent that the correlation (Eq. V-23) provides a reasonable good fit to the experimental data. However, further experimental study is obviously needed to test the correlation developed in this work.

Discussion on the Phase Equilibrium Calculation

Temperature Dependence of Interaction Parameter

From Tables IV and V, and Figures 13 and 14, it can be found that both C_{ij} and D_{ij} has a strong temperature dependency and the trend of such dependency varies from system to system. Both C_{ij} and D_{ij} increases almost linearly with the increase of the temperature. A sudden drop in both C_{ij} and D_{ij} when temperature exceeds 350 ^{o} C is observed in this case. This phenomenon suggests that certain experimental error may be involved in the original experimental data. This may be due to the occurrence of a chemical decomposition or a homogeneous chemical reaction.

Accuracy of K-Value Prediction From Different Set of Mixing Rules

The results of K-value prediction for the two ternary systems have been shown in Tables VII and VIII. It is found that both set of mixing rules works equally well. Both set of mixing rules yields better K-value prediction for hydrogen than that for hydrocarbons. However, it is apparent from Table VI that the first set of mixing rules gives better fitting of binary experimental data than the second one does. Therefore, it seems better to use the first rather than the second set of mixing rules in the multicomponent phase equilibrium calculation. The second set of mixing rules as

used by Twaty and Prausnitz (11) may produce very good binary data fitting for some systems but it also may fail badly for other system as shown in Table VI.

It is further noted that a large portion of deviation in K-value prediction comes from relatively low temperature when either set of mixing rules is used, as shown in Tables X and XI. This indicated that proper weights associating with the experimental uncertainty should be used in binary data fitting.

Discussion on the Reactor Start-up Modeling

Effect of Magnedrive on the Reactor Start-up

The effect of the magnedrive speed on the reactor start-up process is not apparent. However, a high magnedrive speed is necessary in order to reach the perfect mixing state. Such a perfect mixing is important in order for the mathematical model developed in this project to be valid in representing reactor behavior during a single vapor phase stage.

Effect of R_M on the Reactor Start-up

The parameter R_M is the molar feed ratio of hydrocarbon to hydrogen. From Eq. V-11, it is clear that Y_{H2} will reach a steady state value when it is equal to $1 / (R_M + 1)$ or Y_{H2LT}. In other words, it will take infinitely long time

TABLE X

K-VALUE PREDICTION AT DIFFERENT TEMPERATURE
$C_{ij} \neq 0$ and $D_{ij} = 0$

System ID	Temperature °C	Pressure Range atm	Interaction C_{ij}	AADK $_{H2}$	AADK $_{HC}$
1	189.6	20 - 250	0.24	0.6	8.5
	268.7	20 - 250	0.39	1.5	5.7
	348.6	50 - 250	0.53	2.3	3.6
	389.1	50 - 250	0.34	1.0	3.6
4	189.2	20 - 250	0.35	2.1	9.3
	229.1	20 - 250	0.47	2.9	4.8
	269.4	20 - 250	0.41	1.6	4.0
	308.9	30 - 250	0.26	1.0	2.8
9	189.6	20 - 250	0.35	1.0	12.2
	268.7	20 - 250	0.45	0.8	8.5
	348.6	20 - 250	0.62	1.2	6.5
	428.5	30 - 250	0.51	0.7	3.8

TABLE XI

K-VALUE PREDICTION AT DIFFERENT TEMPERATURES
$C_{ij} = 0$ and $D_{ij} \neq 0$

System ID	Temperature °C	Pressure Range atm	Interaction D_{ij}	AADK $_{H2}$	AADK $_{HC}$
1	189.6	20 - 250	0.021	0.7	4.7
	268.7	20 - 250	0.040	2.2	0.6
	348.6	20 - 250	0.072	1.9	2.0
	389.1	20 - 250	0.054	1.4	1.3
4	189.2	20 - 250	0.042	0.8	4.1
	229.1	20 - 250	0.056	1.6	2.2
	269.4	20 - 250	0.063	0.6	1.1
	308.9	30 - 250	0.054	0.6	1.5
9	189.6	20 - 250	0.024	1.6	11.6
	268.7	20 - 250	0.035	1.0	2.6
	348.6	20 - 250	0.060	1.6	1.4
	428.5	30 - 250	0.070	1.6	1.6

for Y_{H2} to reach Y_{H2LT}. This is obvious from Eq. V-14. Since the value of Y_{H2LT} comes from the material balance about the reactor representing the CSTR characteristics of the reactor, it can be viewed as the reactor limited hydrogen mole fraction in vapor phase or RLHMFVP. The change of R_M will result in a change of RLHMFVP as Shown in Figure 15. This change is important in determining whether or not the phase transition will occur as will be discussed next.

Effect of Phase Equilibria on
the Reactor Start-up

When the R_M along with the reactor temperature and pressure is fixed, the system dew point is fixed. To realize the phase transition, the continuously changing Y_{H2} (See Eq. V-13) should equal to the hydrogen mole fraction at the fixed dew point, say Y_{HDEW}. For reactor start-up under pure hydrogen atmosphere, Y_{H2} is continuously decreasing with the limit Y_{H2LT} or RLHMFVP (See Figure 16). When the Y_{HDEW} is lower than Y_{H2LT}, the phase transition can not occur. Therefore, Figure 16 actually serves as the phase transition map. If the Y_{HDEW} is located above the Y_{H2} curve, phase transition will occur, i.e., liquid phase will appear inside the reactor. If the Y_{HDEW} is located below the Y_{H2} curve, the phase transition will not occur and the reactor will operate in a single vapor phase.

Effect of Reaction on
the Reactor Start-up

Although the Eq. V-1 through Eq. V-14 are developed essentially based on non-reactive binary system, it will be a good approximation for a reactive system of a heavy hydrocarbon hydrogenation process. For a reactive system, there are two extreme situations. In one case, the reaction rate is so slow that it can be neglected. In the other case, the reaction is so fast that it can instantaneously convert the reactants to the product as the reactants enter into the reactor. For the slow reaction system, the developed model can be used. For the fast reaction, the reactive system will be at chemical equilibrium. Thus the inlet heavy hydrocarbon can be viewed as non-reactive feed which in turn fits the developed model exactly. For a complex reaction system, proper lumping technique (44) may be needed in order to use the developed model correctly. All the above discussion has concerned only with the Y_{H2}, the role of Y_{HDEW} for reactive systems has not been discussed yet. Whether or not Y_{HDEW} can be obtained by physical phase equilibrium calculation depends on the properties of the reaction products. If the reaction products have significantly different molecular structure and physical properties with respect to the reactants or if a strong interaction exists between the reactants and the products, then Y_{HDEW} can not be calculated purely by a phase equilibrium calculation process. If the

products and the reactants do not differ appreciably from each other, then the products and reactants can be either lumped into one pseudocomponent or kept as separate components and the multicomponent phase equilibrium calculation procedure can be used to calculate Y_{HDEW}.

Effect of Flow Rate on the Reactor Start-up

From Eq. V-14, it is clear that an increase in the total inlet molar rate can significantly affect the time needed to reach the phase transition point if such a point exists at the operating temperature, pressure and R_M. The ratio of Y_{H2} to Y_{HLT} also plays an important role in determining the transition time. When R_M is fixed, the temperature and pressure determine the value of this ratio. The larger this ratio is, the longer is the time needed to reach the transition point. This phenomenon is shown in Figure 20.

the Time Needed for the Reactor to Reach the Steady State

Overall, the time requirement for the reactor to reach its steady state can be calculated based on the previous results of the reactor start-up process modeling, the phase equilibrium calculation and the liquid holdup correlation. The calculation procedure for the time requirement is given as following :

(a). Calculate the dew point hydrogen composition at the specified process condition and check the phase boundary map to see if the reactor is able to reach its dew point. If answer is yes, then go to the next step otherwise stop the calculation.

(b). Calculate the time needed to reach the transition point.

(c). Calculate the time needed to reach the steady state liquid holdup.

(d). Add the results from (b) and (c) to obtain the total time required for the reactor to reach its hydrodynamic steady state.

In a summary, the operation mode and the magnedrive speed have major effects on the flow pattern inside the Berty reactor when the fluid is a vapor-liquid mixture. The steady state liquid holdup does not depend on the magnedrive speed when the magnedrive speed is not less than 1500 rpm. In general, the first set of mixing rules can be used safely in phase equilibrium calculation. The feed molar ratio is an important factor in determining the phase transition. The time needed for the reactor to reach its steady state can be calculated by three steps as discussed above.

CHAPTER VII

ACCOMPLISHMENTS, CONCLUSIONS AND RECOMMENDATIONS

Accomplishments

1. Factors affecting the flow uniformity of a liquid-vapor mixture inside a Berty reactor were identified.
2. Correlations were proposed to estimate the liquid holdup at transient or steady state.
3. Good fitting of the binary experimental data and accurate prediction of K-values of hydrogen and heavy hydrocarbon components in ternary mixtures were obtained. This in turn ensures reliable prediction of phase condition for multicomponent system.
4. The reactor start-up process was modeled and the phase transition point and phase boundary were identified for the reactor operation under different phase condition.

Conclusions

1. When a Berty reactor is operated at continuous mode, the two phase mixture flow inside the reactor is not uniform, even at magnedrive speeds higher than 1500 rpm. But a uniform flow pattern for the two phase mixture can be obtained for magnedrive speeds higher than 100 rpm when the reactor is operated in the batch mode.

The changes in the liquid inlet flow rate and the reactor pressure do not produce any appreciable change in the flow pattern. A change in the inlet gas flow rate does not produce any change in the flow patterns either, however more bubbles are produced at higher gas feed rate.

2. Interaction parameters obtained from binary experimental data fitting are strongly temperature dependent. At different temperatures, different interaction parameters should be used to predict the K-values, if good accuracy is required. At the same temperature range, the fitted interaction parameters can be directly used in ternary phase equilibrium prediction with very good accuracy.
3. Phase transition point and phase boundary are mainly determined by inlet hydrogen and hydrocarbon molar flow rate ratio and the reactor temperature and pressure.
4. Liquid entrainment in the exit gas can be neglected before the hydrodynamic steady state is reached. Thus the unsteady state liquid holdup increases almost linearly with the increase in the operation time after the liquid starts to accumulate inside the reactor.

Recommendations

1. The ratio of the diameter of the catalyst basket to the diameter of the reactor may need to be smaller in order to overcome the non-uniform flow problem when reaction

fluid is a two phase mixture. This should be investigated experimentally.

2. When a kinetic study is conducted in a vapor phase, at least two operation points in the vapor phase region should be selected to test if there is any capillary condensation effect involved.
3. Second set of mixing rules needs to be further tested to see if there is any relation between its applicability and the system characteristics.
4. The actual entrainment can be further measured by adding a tracer that will not evaporate and is soluble in the liquid phase. By measuring the concentration of such a tracer in the exit stream, the liquid entrainment can be evaluated.

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APPENDIX A

EXPERIMENTAL PROCEDURE

The solid-liquid-vapor three-phase hydrodynamic study of an internal recirculation reactor can be divided into two aspects. One is the visual observation of the flow patterns and the other is the measurement of the liquid holdup at the transient and steady state.

Visual Observation of the Flow Patterns

1. Install the catalyst basket.
2. Weigh about 20g glass beads with an average diameter of 3 mm and pour into the catalyst basket.
3. Put the rubber O-ring on the top of the reactor.
4. Replace the original reactor cap with the plexiglass one which has the same dimensions as the original reactor cap.
5. Install the exit line and the thermocouple.
6. Use a small amount of Silver Goop on the threads of the reactor.
7. Tighten each bolt to 20 ft-lbs. Becareful not over tighten, otherwise it will result in cracking of the plexiglass cap.
8. Use the nitrogen gas to pressurize the system to 500

psig to test for any leakage, section by section.

9. Start pumping liquid at the selected flow rate and start the magnedrive at a desired speed.
10. After 150 ml liquid is pumped into the reactor, start the visual observation of the flow patterns of the liquid and gas mixture.
11. After finishing the visual observation, stop the liquid and gas flow, depressurize the system, then remove the plexiglass reactor cap.

Measurement of the Liquid Holdup at Steady State

1. Weigh about 20 g glass beads with an average diameter of 3 mm and pour into the catalyst basket.
2. Install the catalytic basket.
3. Install the stainless steel reactor cap.
4. Test for any gas leakage and make the system leak-proof.
5. Start the gas flow and the magnedrive.
6. After the gas flow rate is adjusted and becomes stable at the desired flow rate, start pumping the liquid into the reactor at the desired flow rate.
7. After 150 ml liquid is pumped into the reactor, stop the liquid flow, stop the magnedrive and turn off the inlet line and exit line simultaneously.
8. Collect the liquid accumulated inside the separation and sample bombs.
9. Use the nitrogen gas to thoroughly purge the separation

and sampling bombs and collect the liquid that is purged out.

10. Close the sample bomb exit valve and slowly open the exit line of the reactor to release the pressure if there is any and then close the exit line.
11. Use the nitrogen gas to purge the separation and sample bombs again and collect the liquid that is purged out into another sample jar.
12. Open the exit port located at the bottom of the reactor and let the liquid drain out of the reactor. Finally use the nitrogen gas to purge the reactor thoroughly to make sure that all the liquid inside the reactor is collected.

the Model Test Measurement

1. Select the liquid flow rate, the gas flow rate and the magnedrive speed.
2. Start the liquid, gas flow and the rotator.
3. Shut off both the inlet and outlet lines when the time reaches the desired value.
4. Use the procedure described in the last section to measure the liquid holdup.
5. If the liquid holdup is not close to or less than the ones measured previously at the same conditions, repeat this procedure allowing a longer time duration.

APPENDIX B

VAPOR-LIQUID PHASE EQUILIBRIUM CALCULATION OF HYDROGEN AND HEAVY HYDROCARBON MIXTURES

Vapor-liquid phase equilibrium calculation of hydrogen and heavy hydrocarbon mixtures using an equation of state approach includes mainly three aspects. First is the calculation of parameters of the equation of state. Second is the calculation of the optimum interaction parameters for the mixtures. Third is the isothermal flash calculation.

For calculating the parameters of the Redlich-Kwong equation of state, subroutines CHUEH, RKJZ and SOAVE are developed. Subroutine CHUEH is used to calculate the parameters of equation of state for hydrogen, a quantum gas. Subroutine RKJZ is used to calculation of the parameters of equation of state for heavy hydrocarbon component. As an option, subroutine SOAVE may be used to calculate the parameters of equation of state for either component. CUBIC and PRESURE are two subroutines called by RKJZ. CUBIC is for numerical solution of a cubic equation. PRESURE is for calculation of saturated vapor pressure of the pure components at different temperatures from various correlations.

For calculating the optimum interaction parameters from

binary experimental data, a program called FITCD is developed. It calls subroutines HYDRO, COMPNT, CUBIC1, MIX, and FUGA. The subroutine MDAT is a binary data files for specific system. The subroutines HYDRO, COMPNT and CUBIC1 have the same function as subroutines CHUEH, RKJZ and CUBIC respectively. Since FITCD is developed at the early stage of this work and used only one time, the original structure is therefore kept unchanged throughout this work.

Isothermal flash calculation is performed by using program STATIC developed in this work. Program STATIC is composed of following subroutines : CHUEH, CRITIC, CUBIC, FLASH, GUESK, PROPTY, PRESURE, RKJZ, SOAVE. Subroutines CHUEH, CUBIC, PRESURE, RKJZ, SOAVE have been described above. The subroutine CRITIC calculates the effective critical properties for the quantum gas, which are required by subroutine CHUEH. Subroutine FLASH is a major subroutine where the isothermal flash calculation is carried out. Subroutine GUESK provides the initial guess of K-value for each component by using Wilson's correlation. Subroutine PROPTY is essentially a data file where all necessary pure component data are stored.

Steps Of Calculation for a and b

1. Calculate the saturated vapor pressure and liquid density from empirical correlation of high accuracy
2. Input two initial guesses of b to calculate two a from

equation of state.

3. Use thus obtained two set of a and b to calculate two saturated vapor densities by solving the cubic equation.
4. Use equality of the fugacity at saturation condition to calculate two a1 for two sets of a, b and corresponding liquid and vapor density. Thus two values of a1 - a are obtained at two corresponding different initial guesses of b.
5. Secant method is then used to update b until the a1 - a satisfies certain criteria.

Some comments About Calculation of a and b

1. Above procedure of calculating a and b is valid for hydrocarbon component at the temperature lower than its critical temperature only. For quantum gas such as hydrogen, calculation of a and b is simple and straight forward and therefore not listed here. When temperature is higher than the critical temperature of the hydrocarbon studied, Soave's procedure is used, which is a direct algebra calculation and therefore not listed here.
2. The critical properties of the hydrocarbon component is essentially not required by the above listed procedure, however, the critical properties are still supplied in the computer program in order to get a good and well bounded initial guess of b.

Steps of Calculation of C_{ij} and D_{ij}

1. Input the binary experimental data.
2. Calculate $_a$ and $_b$ for each component.
3. Input the interval of C_{ij} or D_{ij} and the corresponding increment.
4. Calculate fugacities and K-values at each C_{ij} or D_{ij} and select the one which minimizes the object function.
5. Adjust the interval containing the C_{ij} or D_{ij} and corresponding increment by keeping the C ij or D ij at the midpoint of the range. The total lenth of the interval equals to two times of the previous increment. The new increment equals to one tenth of the previous increment.
6. If the increment is less than the tolerance given, then the C_{ij} or D_{ij} at the last loop is taken as the optimum value. Otherwise go to Step 4 and continue the search.

Comments About the Calculation of C_{ij} and D_{ij}

1. This procedure is a time consuming procedure. However it gives information about the changes of the interaction parameter with the changes of temperatures.
2. Object function is a continuous function of the interaction parameter. C_{ij} is usually less than 1.0 and greater than 0. D_{ij} is usually less than 0.01 and greater than 0.

Steps for the Isothermal Flash Calculation

1. Provide options for bubble point, dew point and isothermal flash calculation.
2. Provide options for temperature or pressure adjustment when bubble or dew point calculation is intended.
3. Assign the component identification number for each component in the mixture.
4. Input T, P and feed composition (mole fraction). T or P may serve as the initial guesses depending on the option selected.
5. Input control variables and tolerances.
6. Calculate a and b as described previously.
7. Provide options for using either mixing rules.
8. Input interaction parameter
9. Provide option for input or calculate initial guesses of the K-values for each component.
10. Use CUBIC to calculate the specific volume of the liquid and vapor mixture at the equilibrium state.
11. Initiating the calculation
12. Use FLASH to calculate the vapor fraction and the K-values.
13. Check the difference between the two consecutively calculated K-values of each component. If the difference is within the tolerance given, go to next step. If not, go to Step 12 by direct substitution of the K-values.

14. Check the difference of vapor fraction obtained from the two cosecutive steps. If it is within the tolerance, go to next step. If not, go to Step 12 by a direct substitution.
15. If the option selected is for the flash calculation, then, calculation is finished. If not, go to the next step.
16. Depending on the option selected for updating the iterative variable, one may need go back to step 6 if temperature is being updated or go back to step 8 if pressure is being updated.

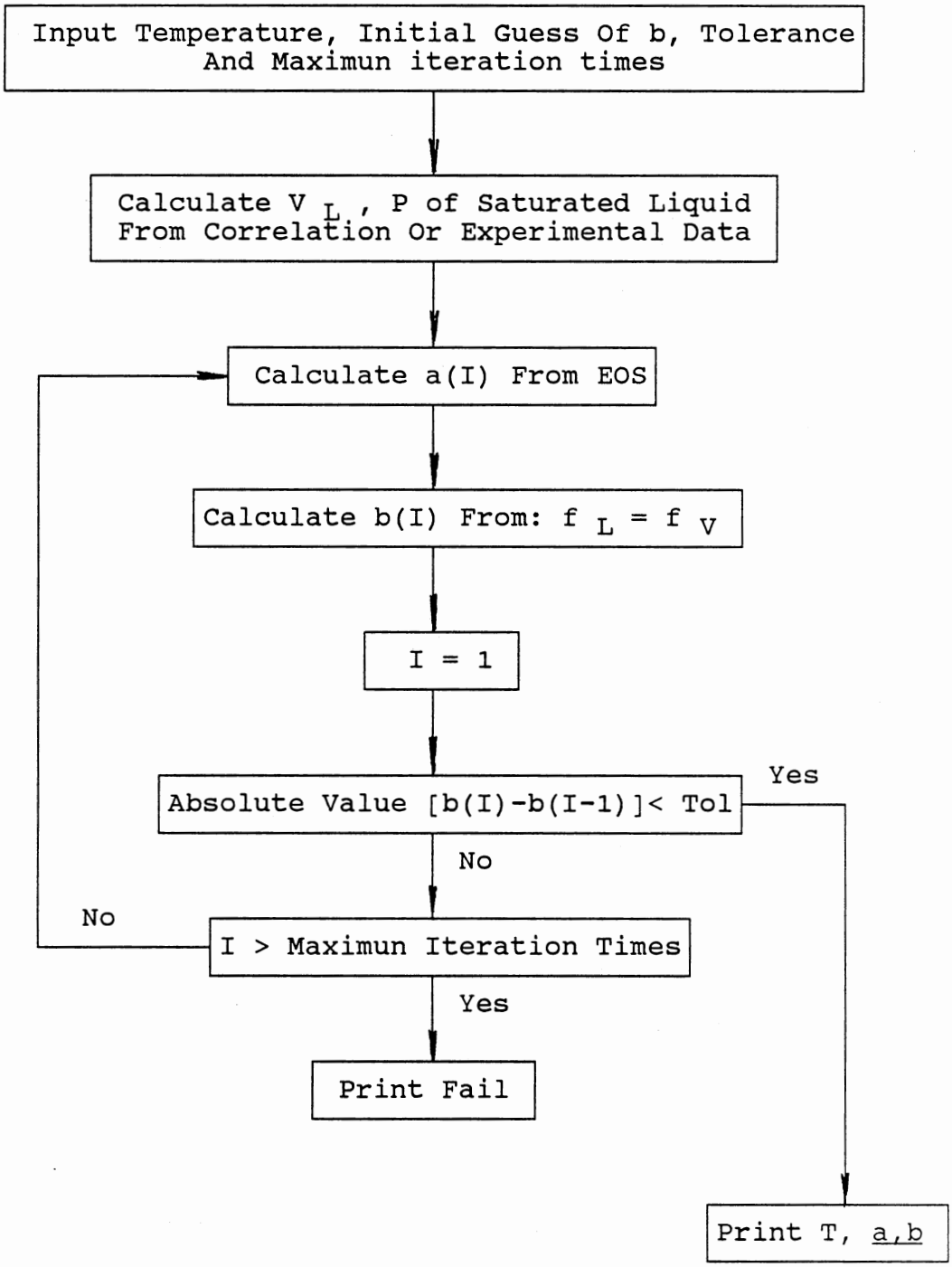
Comments About the Isothermal Flash Calculation

1. Dew point and bubble point calculation need to be done before proceeding to the flash calculation in order to avoid making the flash calculation in a single phase, which usually will result in non-convergenc problem.
2. The first set of mixing rules is usually prefered in making all the phase equilibrium calculations. The second set of mixing rules should be used with causion.
3. Subroutine GUESK can be used to obtain the initial gusee of K-values for the components involved in the mixture when the mixture is far away from it critical point. Otherwise, input initial guess of the K-value for each component is necessary.

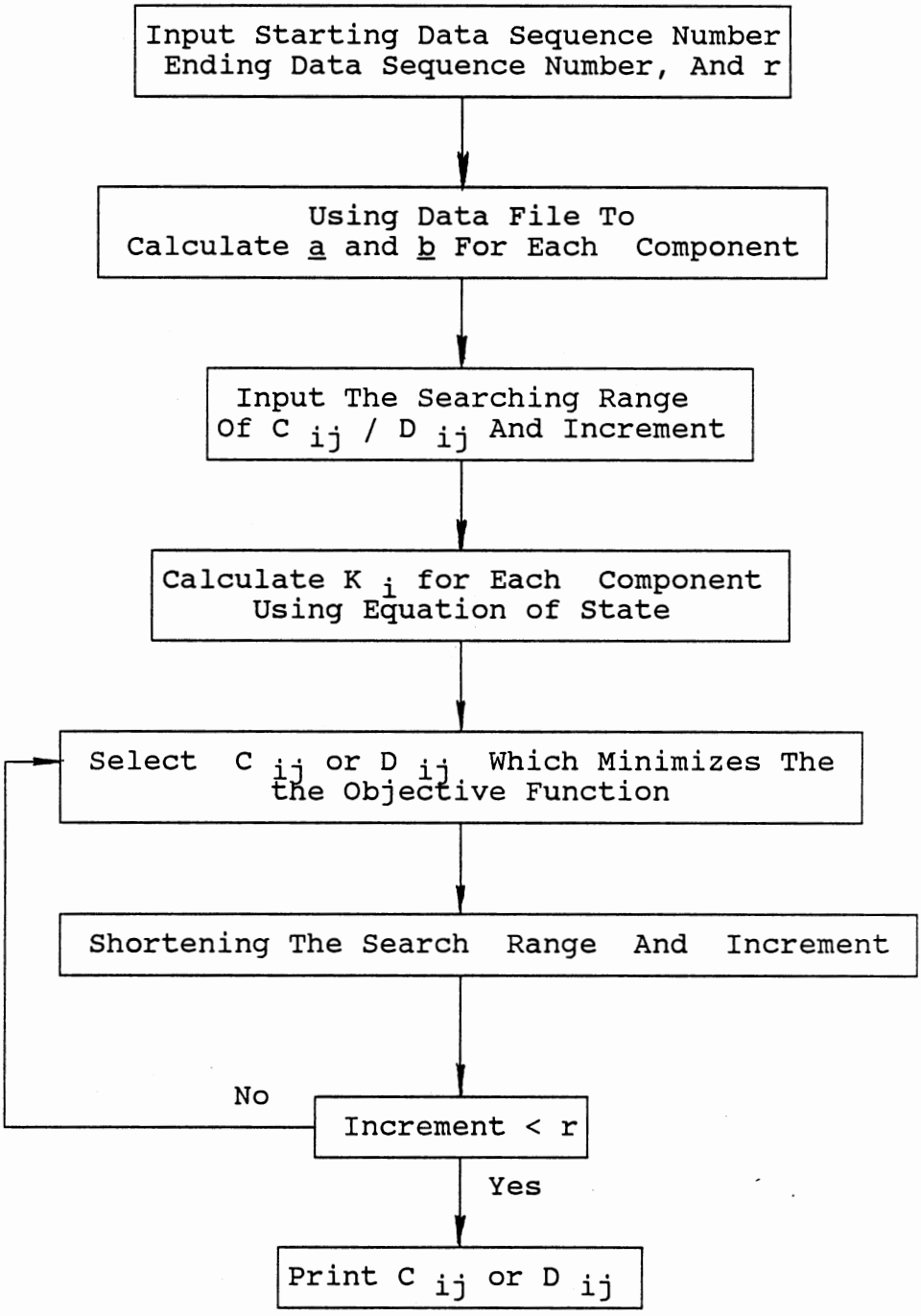
APPENDIX C

COMPUTATION FLOW SHEETS AND COMPUTER PROGRAM

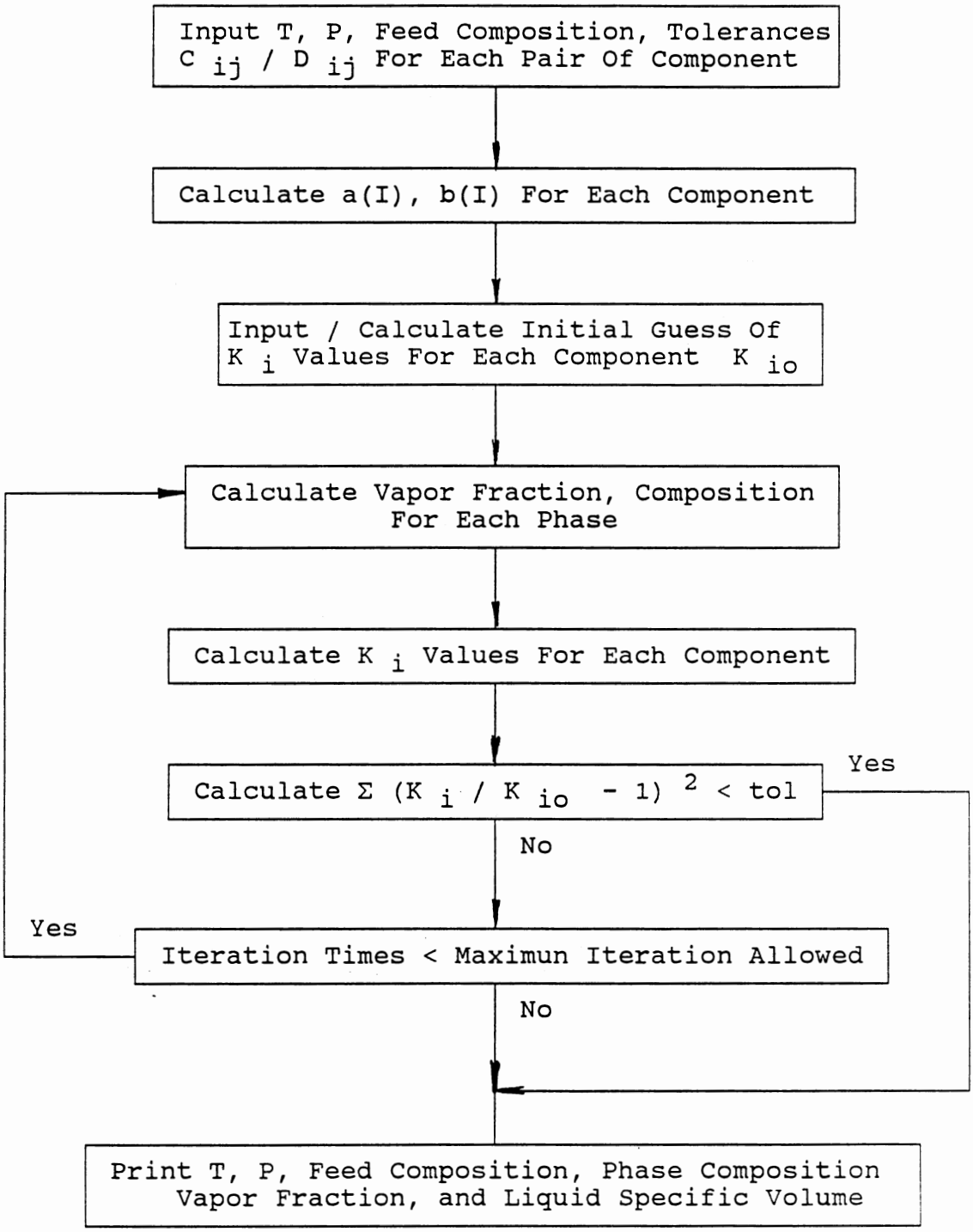
Flow Sheet of a and b Calculation



Flow Sheet of Calculation of Optimun C_{ij} or D_{ij}



Flow Sheet of Multicomponent Isothermal Flash Calculation



```
      SUBROUTINE CRITIC(I,T,TCQUN,PCQUN)
C     THIS SUBROUTINE IS FOR CONVERSION OF CRITICAL
C     PROPERTIES OF QUANTUM GAS TO ITS EFFECTIVE CRITICAL
C     PROPERTIES AND THIS SUBROUTINE IS USED TOGETHER WITH
C     SUBROUTINE CHUEH FOR EOS PARAMETERS CALCULATION OF QUANTUM GAS
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON /FIRST/
      ID(10),TC(20),PC(20),W(20),WM(20),VSTR(20)
      TCQUN=TC(I)/(1.0+21.8/WM(I)/(T+273.15))-273.15
      PCQUN=PC(I)/(1.0+44.2/WM(I)/(T+273.15))
      RETURN
      END

      SUBROUTINE CHUEH(TCQUN,PCQUN,AQUN,BQUN,ICONV)
C     THIS SUBROUTINE IS FOR CALCULATION OF PARAMETERS A
C     AND B OF RK EOS FOR HYDROGEN USING CHUEH'S PROCEDURE
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON /THIRD/ ITM,NCOMP,R,TOL
      AQUN=0.4278*R*R*((TCQUN+273.15)**2.5)/PCQUN
      BQUN=0.0867*R*(TCQUN+273.15)/PCQUN
      ICONV=0
      RETURN
      END

      SUBROUTINE CUBIC(IPH,AA,BB,P,T,ZCAL,ICONV)
C     THIS SUBROUTINE SOLVES A CUBIC EQUATION USING
C     ITERATIVE PROCEDURE IN WHICH THE INITIAL GUESS
C     IS GIVEN BY A SEQUENTIAL SEARCH IN THE MOST
C     POSSIBLE RANGE AND IS BOUNDED BY THE NUMBER OF ROOTS
C     OR BY THE PHSYCAL MEANINGFUL RANGE
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON /THIRD/ ITM,NCOMP,R,TOL
C     CALCULATION DIMENSIONLESS PARAMETER FOR EOS
      C1=AA*P*((T+273.15)**(-2.5))/R/R
      C2=BB*P/R/(T+273.15)
      QZ=C1-C2-C2*C2
      RZ=C1*C2
      ICONV=0
      IROOT=1
C     SET THE SEARCHING RANGE
      IF(IPH.EQ.1) THEN
      Z0=0.8
      ZEND=1.2
      ELSE IF(IPH.EQ.2) THEN
      Z0=0.1
      ZEND=0.5
      END IF
      DZ0=0.1
100   J=0
      Z=Z0
150   F0=Z*Z*Z-Z*Z+QZ*Z-RZ
      F1=3.0*Z*Z-2.0*Z+QZ
      DELTZ=F0/F1
      IF(DABS(DELTZ).GT.1.0) THEN
```

```
      DELTZ=0.01*DELTZ/DABS(DELTZ)
      END IF
      Z=Z-DELTZ
      IF(DABS(F0/F1).LT.TOL) THEN
      ICONV=0
      GO TO 200
      END IF
      J=J+1
      IF(J.GT.(ITM+100)) THEN
      ICONV=1
      GO TO 200
      ELSE IF(J.LE.ITM) THEN
      GO TO 150
      END IF
200   IF(Z.LE.C2.OR.ICONV.EQ.1) GO TO 250
      IF(IROOT.EQ.1) THEN
C     SHORTEN THE RANGE AND CONTINUE SEARCHING
      ZCAL=Z
      IROOT=IROOT+1
      GO TO 250
      END IF
      IF(IPH.EQ.1) THEN
      ZCAL=DMAX1(ZCAL,Z)
      IROOT=IROOT+1
      GO TO 250è       ELSE IF(IPH.EQ.2) THEN
      ZCAL=DMIN1(ZCAL,Z)
      IROOT=IROOT+1
      GO TO 250
      END IF
C     CHECK THE NUMBER OF DIFFERENT SOLUTIONS
C     SO FAR OBTAINED
250   IF(IROOT.GT.3) GO TO 300
      Z0=Z0+DZ0
      IF(Z0.GT.ZEND) THEN
      GO TO 300
      ELSE
      GO TO 100
      END IF
300   IF(ZCAL.LE.C2) THEN
      ICONV=1
      ELSE
      ICONV=0
      END IF
      RETURN
      END

      PROGRAM FITCD
C     THIS PROGRAM IS FOR FITTING THE INTERACTION PARAMETERS
C     Cij OR Dij. THE PROGRAM HAS SIX EXTERNALS WHICH ARE
C     SHORT SUBROUTINES. HYDRO, COMPNT, CUBIC1 ARE SIMILAR TO
C     CHUEH, RKJZ, CUBIC RESPECTIVELY WHILE MDAT, MIX,
C     AND FUGA ARE IN ORDER DATA FILE, CALCULATION OF EOS
C     PARAMETER FOR MIXTURE AND CALCULATION OF GUGACITIES FOR
C     EACH COMPONENT INVOLVED. THIS IS THE ONE OF OF THE TWO
```

```
C       FITTING PROGRAMS AND ALL INFORMATION OF EXPERIMENTAL RESULTS
C       ARE USED IN DIRECT FITTING PROCESS.
        IMPLICIT REAL*8(A-H,O-Z)
        DIMENSION BW(200),FAB(200)
        COMMON T,R,ITM,TOL
C       INPUT CONTROL VARIABLES AND RANGE OF FITTING
        EXTERNAL MDAT4,HYDRO,COMPNT4,CUBIC1,MIX,FUGA
        WRITE(*,100)
        READ(*,*) R,ITM,TOL,IFIT,CDLOW,CDHIGH,DELTCD,NDT1,NDT2,ICOMP
        OPTIMF=1000.0
        CD=CDLOW
        CDBOUND=CDHIGH
C       START FITTING AT SELECTED FITTING RANGE AND INCREMENT
10      CD=CD+DELTCD
        IF(IFIT.EQ.1) THEN
        CC=CD
        DD=0.0
        ELSE
        CC=0.0
        DD=CD
        END IF
        AADKT=0.0
        AADKH=0.0
        OBJF=0.0
        NDAT=NDT2-NDT1+1
        IDAT=NDT1
20      CALL MDAT4(IDAT,T,P,EXH,EYH,EKH,EKT,IDTRNGE)
        IF(IDTRNGE.EQ.1) GO TO 40
        YT=DBLE(1.0)-EYH
        XT=DBLE(1.0)-EXH
        YH=EYH
        XH=EXH
C       CALCULATE EOS PARAMETERS FOR MIXTURE
        CALL HYDRO(AH,BH)
        CALL COMPNT4(AT,BT,ICONV1)
        IF(ICONV1.NE.0) GO TO 40
        DO 30, I=1,2
        IF(I.EQ.1) THEN
        Z=YT
        ELSE IF(I.EQ.2) THEN
        Z=XT
        END IF
        CALL MIX(AT,BT,AH,BH,CC,DD,AM,BM,AAH,BBH,Z)
C       SOLVE FOR VAPOR AND LIQUID DENSITIES
        CALL CUBIC1(I,P,AM,BM,V,ICONV2)
        IF(ICONV2.GE.1) GO TO 40
        DO 30, J=1,2
        IF(I.EQ.1.AND.J.EQ.1) THEN
        E=YT*AT+(1.0-YT)*AAH
        E1=2.0*(YT*BT+(1.0-YT)*BBH)-BM
C       CALCULATE FUGACITIES FOR EACH COMPONENTS
        CALL FUGA(P,V,AM,BM,E,E1,FUGTV,ICONV3)
        END IF
        IF(ICONV3.GE.1) GO TO 40
```

```
      IF(I.EQ.1.AND.J.EQ.2) THEN
      E=YH*AH+(1.0-YH)*AAH
      E1=2.0*(YH*BH+(1.0-YH)*BBH)-BM
      CALL FUGA(P,V,AM,BM,E,E1,FUGHV,ICONV3)
      END IF
      IF(ICONV3.GE.1) GO TO 40
      IF(I.EQ.2.AND.J.EQ.1) THEN
      E=XT*AT+(1.0-XT)*AAH
      E1=2.0*(XT*BT+(1.0-XT)*BBH)-BM
      CALL FUGA(P,V,AM,BM,E,E1,FUGTL,ICONV3)
      END IF
      IF(ICONV3.GE.1) GO TO 40
      IF(I.EQ.2.AND.J.EQ.2) THEN
      E=XH*AH+(1.0-XH)*AAH
      E1=2.0*(XH*BH+(1.0-XH)*BBH)-BM
      CALL FUGA(P,V,AM,BM,E,E1,FUGHL,ICONV3)
      END IF
      IF(ICONV3.GE.1) GO TO 40
30    CONTINUE
C     CALCULATE AVERAGE ABSOLUTE DEVIATION IN K VALUE
C     FOR EACH COMPONENT AND CALCULATE THE VALUE OF OBJECTIVE FUNCTION
      RKT=FUGTL/FUGTV
      RKH=FUGHL/FUGHV
      DKT=DABS((RKT-EKT)/EKT)/DBLE(NDAT)
      DKH=DABS((RKH-EKH)/EKH)/DBLE(NDAT)
      FRKT=(XT*FUGTL-YT*FUGTV)*(XT*FUGTL-YT*FUGTV)
      FRKH=(XH*FUGHL-YH*FUGHV)*(XH*FUGHL-YH*FUGHV)
      OBJF=(FRKT+FRKH)**0.5+OBJF
      AADKT=AADKT+DKT
      AADKH=AADKH+DKH
      IF(IDAT.LT.NDT2) THEN
      IDAT=1+IDAT
      GO TO 20
      END IF
C     SAVE TEMPERALY BEST INTERACTION PARAMETER
      IF(OPTIMF.GT.OBJF) THEN
      OPTIMF=OBJF
      OPTIMCD=CD
      OPADKH=AADKH
      OPADKT=AADKT
      WRITE(*,200) IFIT,OPTIMCD,OPTIMF,OPADKT,OPADKH
      END IF
C     ADJUST FITTING RANGE AND INCREMENT
      IF(CD.LT.CDBOUND) GO TO 10
      CD=OPTIMCD-DELTCD
      CDBOUND=OPTIMCD+DELTCD
      DELTCD=0.1*DELTCD
      IF(IFIT.EQ.1.AND.DELTCD.GE.0.001) GO TO 10
      IF(IFIT.EQ.2.AND.DELTCD.GE.0.0001) GO TO 10
C     OUTPUT THE OPTIMUM INTERACTION PARAMETER
      WRITE(*,300) IFIT,OPTIMCD,OPTIMF,OPADKT,
1     OPADKH,NDT1,NDT2,NDAT,ICOMP
      GO TO 50
40    WRITE(*,400)
```

```
50      STOP
100     FORMAT(2X,'IFIT = 1 : FIT OPTIMUN C-VALUE'/
        1 2X,'IFIT = 2 : FIT OPTIMUN D-VALUE'/
        2 2X,'READ R,ITM,TOL,IFIT,CDLOW,CDHIGH,'/
        3 2X,'DELTCD,NDT1,NDT2,ICOMP')
200     FORMAT(2X,'IFIT =',I2,1X,'CD =',D10.4,1X,'OBJF =',D10.4,
1       1X,'AADKT =',D10.4,1X,'AADKH =',D10.4)
300     FORMAT(//2X,'CALCULATION RESULTS FROM CDFIT1 :'/
        1 2X,'IFIT=',I5/
        2 2X,'OPTIMUM   C  OR D    VALUE       =',D10.5/
        3 2X,'OBJECT    FUNCTION   VALUE       =',D10.5/
        4 2X,'ABSOLUTE AVERAGE DEVIATION IN KT =',D10.5/
        5 2X,'ABSOLUTE AVERAGE DEVIATION IN KH =',D10.5/
        6 2X,'STARTING DATA SEQUENCE NUMBER    =',I5/
        7 2X,'ENDING   DATA SEQUENCE NUMBER    =',I5/
        8 2X,'TOTAL    DATA USED IN FITTING    =',I5/
        9 2X,'COMPNT IDENTIFICATION  NUMBER    =',I5)
400     FORMAT(2X,'CALCULATION FAILED'/)
        END

        SUBROUTINE FLASH(T,P,FV,KIND3,ICNTRL,ITER)
C       THIS SUBROUTINE IS FOR ISOTHERMAL FLASH CALCULATION AND
C       IS MAJOR SUBROUTINE IN THE MAIN PROGRAM STATIC
        IMPLICIT REAL*8(A-H,O-Z)
        DIMENSION SUMF(120),FF(10)
        COMMON /FIRST/ ID(10),TC(20),PC(20),W(20),WM(20),VSTR(20)
        COMMON /SECOND/ V(2,10),A(10),B(10),C(10,10),
        1 D(10,10),FUGAC(2,10)
        COMMON /THIRD/ ITM,NCOMP,R,TOL
        COMMON /FIFTH/ Z(10),X(2,10),CK(10)
        EXTERNAL CUBIC
        ITER=1
        KIND3=0
        ICNTRL=0
        ICNTRL1=0
        ICNTRL2=0
C       NORMALIZATION OF MOLAR FRACTION
10      SUMX=0.0
        SUMY=0.0
        DO 20 I=1,NCOMP
        SUMX=SUMX+Z(I)/CK(I)
        SUMY=SUMY+Z(I)*CK(I)
20      CONTINUE
C       CHECK PHASE CONDITION
        IF(SUMY.GT.1.0.AND.SUMX.GT.1.0) THEN
        ICASE=1
        ELSE IF(SUMY.LT.1.0) THEN
        ICASE=2
        ELSE IF(SUMX.LT.1.0) THEN
        ICASE=3
        END IF
        IF(ITER.EQ.1) THEN
        FV=0.5
        GO TO 40
```

```
      END IF
      IF(ICASE.EQ.3) THEN
      FV=1.0
      GO TO 40
      ELSE IF(ICASE.EQ.2) THEN
      FV=0.0
      GO TO 40
      END IF
C     CALCULATE VAPOR FRACTION AFTER FLASH
      G=0.0
      G1=0.0
      DO 30 I=1,NCOMP
      C6=1.0+FV*(CK(I)-1.0)
      C7=C6*C6
      G=G+Z(I)*(CK(I)-1.0)/C6
      G1=G1+Z(I)*(CK(I)-1.0)*(CK(I)-1.0)/C7
30    CONTINUE
      DFV=G/G1
      IF(DABS(DFV).LT.TOL) GO TO 40
      IF(DABS(DFV).GT.1.0) THEN
      DFV1=0.01
      DFV=DSIGN(DFV1,DFV)
      END IF
      FV=FV+DFV
      IF(FV.LT.0.0001) THEN
      FV=0.0
      ELSE IF(FV.GT.0.9999) THEN
      FV=1.0
      END IF
40    DO 50 I=1,NCOMP
      X(2,I)=Z(I)/(1.0+FV*(CK(I)-1.0))
      X(1,I)=CK(I)*Z(I)/(1.0+FV*(CK(I)-1.0))
C     CALCULATE PHASE COMPOSITION
50    CONTINUE
      COMPX=0.0
      COMPY=0.0
      DO 60 I=1,NCOMP
      COMPX=X(2,I)+COMPX
      COMPY=X(1,I)+COMPY
60    CONTINUE
      DO 70 I=1,NCOMP
      X(1,I)=X(1,I)/COMPY
      X(2,I)=X(2,I)/COMPX
70    CONTINUE
C     CALCULATION OF K VALUE OF EACH COMPONENT
      M=NCOMP+1
      DO 120 K=1,2
      IF(KIND3.NE.0) GO TO 120
      AM=0.0
      BM=0.0
      DO 90 I=1,NCOMP
      DO 80 J=1,NCOMP
      AM=X(K,I)*X(K,J)*(1.0-C(I,J))*
     1 (A(I)*A(J))**0.5+AM
```

```
      BM=0.5*X(K,I)*X(K,J)*(B(I)+B(J))*(1.0+D(I,J))+BM
80    CONTINUE
90    CONTINUE
      A(M)=AM
      B(M)=BM
C     VAPOR AND LIQUID DENSITY CALCULATION
      CALL CUBIC(K,AM,BM,P,T,ZCUBIC,ICONV)
      IF(ICONV.EQ.1) THEN
      KIND3=2
      GO TO 120
      END IF
      VM=ZCUBIC*R*(T+273.15)/P
      V(K,M)=VM
      C3=VM/(VM-BM)
      C4=ZCUBIC
      C5=(VM+BM)/VM
      IF(VM.LE.10.0D-8) THEN
      KIND3=3
      ELSE IF(C3.LE.10.0D-8) THEN
      KIND3=4
      ELSE IF(C4.LE.10.0D-8) THEN
      KIND3=5
      ELSE IF(C5.LE.10.0D-8) THEN
      KIND3=6
      END IF
      IF(KIND3.NE.0) GO TO 120
      DO 110 I=1,NCOMP
      IF(KIND3.NE.0) GO TO 110
      SUM1=0.0
      SUM2=0.0
      DO 100 J=1,NCOMP
      SUM1=SUM1+2.0*X(K,J)*(1.0-C(I,J))*
     1 (A(I)*A(J))**0.5
      SUM2=SUM2+X(K,J)*(1.0+D(I,J))*(B(I)+B(J))
100   CONTINUE
C     FUGACITY CALCULATION USING EOS
      FUG=DLOG(C3)+(SUM2-BM)/(VM-BM)-DLOG(C4)-
     1 SUM1*DLOG(C5)/BM/R/((T+273.15)**
     2 1.5)+AM*(SUM2-BM)*(DLOG(C5)-BM/(VM+BM))/
     3 R/((T+273.15)**1.5)/BM/BM
      IF(DABS(FUG).GT.10.D+6.OR.DABS(FUG).LT.10.D-6) THEN
      KIND3=7
      GO TO 110
      END IF
      FUGAC(K,I)=DEXP(FUG)
110   CONTINUE
120   CONTINUE
      IF(KIND3.NE.0) GO TO 120
      SUMFF=0.0
      DO 130 I=1,NCOMP
      FF(I)=FUGAC(2,I)/FUGAC(1,I)/CK(I)
      CK(I)=FUGAC(2,I)/FUGAC(1,I)
      SUMFF=SUMFF+(FF(I)-1.0)*(FF(I)-1.0)
130   CONTINUE
```

```
      SUMF(ITER)=SUMFF
C     CHECK THE CONVERGENCE OF K VALUE
      IF(SUMFF.LT.0.000001) THEN
      KIND3=0
      ICNTRL1=1
      GO TO 150
      END IF
      IF(ITER.EQ.1) GO TO 140
C     CHECK THE PHASE CONDITION SEE IF IT IS SINGLE PHASE
      SUMFR=SUMF(ITER)/SUMF(ITER-1)-1.0
      IF(DABS(SUMFR).LT.0.0001) THEN
      KIND3=0
      ICNTRL2=1
      GO TO 150
      END IF
140   ITER=ITER+1
      IF(ITER.LE.(ITM+100)) GO TO 10
      KIND3=8
C     TRANFER INFORMATION OF PHASE CONDITION BACK TO MAIN PROGRAM
150   IF(ICNTRL1.EQ.1.AND.ICNTRL2.EQ.1) THEN
      ICNTRL=3
      ELSE IF(ICNTRL1.EQ.1.AND.ICNTRL2.NE.1) THEN
      ICNTRL=1
      ELSE IF(ICNTRL1.NE.1.AND.ICNTRL2.EQ.1) THEN
      ICNTRL=2
      END IF
      RETURN
      END

      SUBROUTINE GUESK(T,P,CK)
C     THIS SUBROUTINE IS FOR CALCULATION OF K VALUE AS INITIAL GUESS.
C     FOLLOWING IS THE CALCULATION BASE ON WILSON'S PROCEDURE AND THIS
C     SUBROUTINE CAN BE EXPANDED IF THEIR ANY BETTER CORRELATION
C     FOR CALCULATING K VALUE IS AVAILABLE
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION CK(10)
      COMMON /FIRST/ID(10),TC(20),PC(20),W(20),WM(20),VSTR(20)
      COMMON /THIRD/ ITM,NCOMP,R,TOL
      DO 10 I=1,NCOMP
      CK(I)=5.37*(1.0+W(I))*(1.0-(TC(I)+273.15)/(T+273.15))
      CK(I)=(PC(I)/P)*DEXP(CK(I))
10    CONTINUE
      RETURN
      END

      SUBROUTINE PRESURE(I,TR,T,P)
C     THIS SUBROUTINE IS FOR PURE COMPONENT VAPOR PRESSURE CALCULATION
C     WHICH IS NECCESARRY IN CALCULATION OF PARAMETERS OF EOS IN RKJZ.
C     THIS SUBROUTINE CAN BE EXPANDED WHEN NEW COMPONENT IS
C     ENCOUNTEERED IN THE FLASH CALCULATION. ALSO THE CORRELATION
C     CAN BE NMODIFIED IF NEW AND BETTER CORRELATION IS AVAILABLE.
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON /FIRST/ ID(10),TC(20),PC(20),W(20),WM(20),VSTR(20)
      IF(ID(I).LE.10) GO TO 1000
```

```
      IF(ID(I).EQ.11) GO TO 110
      IF(ID(I).EQ.12) GO TO 120
      IF(ID(I).EQ.13) GO TO 130
      IF(ID(I).EQ.14) GO TO 140
      IF(ID(I).EQ.15) GO TO 150
110   IF(T.LT.140.0) THEN
      P=4.20046-1735.82/(206.361+T)
      ELSE IF(T.LE.220.AND.T.GE.140.) THEN
      P=4.10276-1664.78/(198.721+T)
      ELSE IF(T.GE.220.) THEN
      P=-23.5783+55.7829*TR+1.477/TR-50.8029*TR*TR+
     1 17.0558*TR*TR*TR+0.0722179*DLOG10(TC(I)+
     2 8-T)+DLOG10(PC(I)/0.9869233)
      END IF
      GO TO 900
120   IF(T.LE.250) THEN
      P=4.00078-1595.602/(203.576+T)
      ELSE IF(T.GT.250.) THEN
      P=21.05311-6.75466/TR-32.42153*TR+25.73996*TR*TR-
     1 7.61687*TR*TR*TR-8.94341*DLOG10(TC(I)+
     2 8-T)*10.**(-4.0)+DLOG10(PC(I)/0.9869233)
      END IF
      GO TO 900
130   IF(T.LE.240) THEN
      P=3.99190-1572.778/(207.248+T)
      ELSE IF(T.GT.240) THEN
      P=4.10844-3.66099/TR+1.5796*TR-3.91707*TR*TR+
     1 1.87001*TR*TR*TR+0.0001*0.223531*DLOG10(TC(I)+8-T)+
     2 DLOG10(PC(I)/0.9869233)
      END IF
      GO TO 900
140   IF(DABS(T-188.0).LT.0.1) THEN
      P=0.143
      ELSE IF(DABS(T-268.0).LT.1.0) THEN
      P=1.088
      ELSE IF(DABS(T-348.0).LT.1.0) THEN
      P=4.726
      ELSE IF(DABS(T-428.0).LT.1.0) THEN
      P=13.33
      END IF
      GO TO 1000
150   XX=1.0-TR
      PVPC=(-7.59222*XX+1.39441*XX**1.5-3.22746*XX**3.0
     1 -2.40376*XX**6.0)/TR
      PVPC=DEXP(PVPC)
      P=PVPC*PC(I)
      IF(DABS(T-189.25).LT.1.0) THEN
      P=3.15618
      ELSE IF(DABS(T-229.15).LT.1.0) THEN
      P=6.86899
      ELSE IF(DABS(T-269.45).LT.1.0) THEN
      P=13.0373
      ELSE IF(DABS(T-308.95).LT.1.0) THEN
      P=22.3933
```

```
      END IF
      GO TO 1000
900   P=0.9869233*10.**(P)
1000  RETURN
      END

      SUBROUTINE PROPTY(I,TTC,PPC,WW,WWM,VVSTR)
C     THIS SUBROUTINE ESSENTIALLY SERVES AS A BASIC DATA FILE.
C     NOT ALL THE DATA ARE GOING TO BE USED IN THE MAIN PROGRAM,
C     HOWEVER IT SERVES AS DATA BASE IN CASE OF NEED IN CALCULATION
C     FIVE DATA ARE GIVEN HERE. THEY ARE CRITICAL TEMPERATURE,
C     CRITICAL PRESSURE, ACENTRIC FACTOR, MOLECULAR WEIGHT AND
C     CHARACTERISTIC VOLUME PARAMETER USED IN HANKINSON-THOMOSON
C     LIQUID DENSITY CORRELATION.
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON /FIRST/ ID(10),TC(20),PC(20),W(20),WM(20),VSTR(20)
      IF(ID(I).GT.10) GO TO 110
      IF(ID(I).EQ.1) THEN
      TTC=43.6
      PPC=20.2
      WW=0
      WWM=2.0
      VVSTR=0.0
      GO TO 900
      END IF
110   IF(ID(I).EQ.11) THEN
      TTC=447.
      PPC=33.0*0.9869233
      WW=0.297
      WWM=132.2048
      VVSTR=0.4276
      GO TO 900
      ELSE IF(ID(I).EQ.12) THEN
      TTC=429.1
      PPC=32.0*.9869233
      WW=0.286
      WWM=138.2522
      VVSTR=0.47988
      GO TO 900
      ELSE IF(ID(I).EQ.13) THEN
      TTC=413.9
      PPC=28.*0.9869233
      WW=0.25
      WWM=138.2522
      VVSTR=0.4869
      GO TO 900
      ELSE IF(ID(I).EQ.14) THEN
      TTC=496.85
      PPC=28.226
      WW=0.442
      WWM=150.
      VVSTR=0.5751
      GO TO 900
      ELSE IF(ID(I).EQ.15) THEN
```

```
      TTC=343.95
      PPC=34.94
      WW=0.327
      WWM=150.
      VVSTR=0.3731
      GO TO 900
      END IF
900   RETURN
      END

      SUBROUTINE PROPTY(I,TTC,PPC,WW,WWM,VVSTR)
C     THIS SUBROUTINE ESSENTIALLY SERVES AS A BASIC DATA FILE.
C     NOT ALL THE DATA ARE GOING TO BE USED IN THE MAIN PROGRAM,
C     HOWEVER IT SERVES AS DATA BASE IN CASE OF NEED IN CALCULATION
C     FIVE DATA ARE GIVEN HERE. THEY ARE CRITICAL TEMPERATURE,
C     CRITICAL PRESSURE, ACENTRIC FACTOR, MOLECULAR WEIGHT AND
C     CHARACTERISTIC VOLUME PARAMETER USED IN HANKINSON-THOMOSON
C     LIQUID DENSITY CORRELATION.
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON /FIRST/ ID(10),TC(20),PC(20),W(20),WM(20),VSTR(20)
      IF(ID(I).GT.10) GO TO 110
      IF(ID(I).EQ.1) THEN
      TTC=43.6
      PPC=20.2
      WW=0
      WWM=2.0
      VVSTR=0.0
      GO TO 900
      END IF
110   IF(ID(I).EQ.11) THEN
      TTC=447.
      PPC=33.0*0.9869233
      WW=0.297
      WWM=132.2048
      VVSTR=0.4276
      GO TO 900
      ELSE IF(ID(I).EQ.12) THEN
      TTC=429.1
      PPC=32.0*.9869233
      WW=0.286
      WWM=138.2522
      VVSTR=0.47988
      GO TO 900
      ELSE IF(ID(I).EQ.13) THEN
      TTC=413.9
      PPC=28.*0.9869233
      WW=0.25
      WWM=138.2522
      VVSTR=0.4869
      GO TO 900
      ELSE IF(ID(I).EQ.14) THEN
      TTC=496.85
      PPC=28.226
      WW=0.442
```

```
      WWM=150.
      VVSTR=0.5751
      GO TO 900
      ELSE IF(ID(I).EQ.15) THEN
      TTC=343.95
      PPC=34.94
      WW=0.327
      WWM=150.
      VVSTR=0.3731
      GO TO 900
      END IF
900   RETURN
      END

      SUBROUTINE RKJZ(I,AA,BB,VG,VL,ICONV)
C     THIS IS THE JOFFE-ZUDKEVICH PROCEDURE TO CALCULATE EOS
C     PARAMETERS. HERE THE SECANT METHOD IS USED WHILE NEWTON
C     METHOD IS ALSO CAN BE USED. THE EXTERNALS FOR THIS SUBROUTINE
C     PRESURE AND CUBIC TWO SUBROUTINES. THE FUNCTION OF SUBROUTINE
C     PRESURE IS TO CALCULATE PURE VAPOR PRESSURE FOR DIFFERENT
C     COMPONENTS AND FUNCTION OF SUBROUTINE CUBIC IS SIMPLY TO
C     SOLVE FOR DENSITY OF LIQUID OR VAPOR.
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION BW(120),FAB(120)
      COMMON /FIRST/ ID(10),TC(20),PC(20),W(20),WM(20),VSTR(20)
      COMMON /SECOND/ V(2,10),A(10),B(10),C(10,10),
      1 D(10,10),FUGAC(2,10)
      COMMON /THIRD/ ITM,NCOMP,R,TOL
      COMMON /FORTH/ T,GESB1,GESB2
      EXTERNAL PRESURE,CUBIC
      TR=(T+273.15)/(TC(I)+273.15)
C     CALCULATION OF SATURATED PURE LIQUID MOLAR SPECIFIC VOLUME
C     FROM HAMKINSON-THOMOSON CORRELATION
      V1=1.0-1.52816*(1.0-TR)**(1.0/3.0)+1.43907*(1.0-TR)**(2.0/3.0)
      1 -0.81446*(1.0-TR)+0.190454*(1.0-TR)**(4.0/3.0)
      V2=(-0.296123+0.386914*TR-0.0427258*TR*TR-0.0480645*TR**3.0)
      1 /(TR-1.00001)
      VL=VSTR(I)*V1*(1.0-W(I)*V2)
      IF(VL.LE.0.0) THEN
      ICONV=1
      GO TO 400
      END IF
C     CALCULATE PURE COMPONET VAPOR PRESSURE
      CALL PRESURE(I,TR,T,P)
      IF(P.LE.0.0) THEN
      ICONV=2
      GO TO 400
      END IF
      ITM1=ITM+100
C     START ITERATION PROCESS TO SOLVE A AND B
      DO 100,J=1,ITM1
      IF(J.EQ.1) THEN
      BW(J)=GESB1
      ELSE IF(J.EQ.2) THEN
```

```
      BW(J)=GESB2
      END IF
      BB=BW(J)*R*(TC(I)+273.15)/PC(I)
      AA=(R*(T+273.15)/(VL-BB)-P)*VL*(VL+BB)*(T+273.15)**(0.5)
      AW=AA*PC(I)*(R**(-2.0))*(TC(I)+273.15)**(-2.5)
      IPH=1
C     VAPOR AND LIQUID DENSITY CALCULATION
      CALL CUBIC(IPH,AA,BB,P,T,ZCUBIC,ICONV)
      IF(ICONV.EQ.1) GO TO 400
      VG=ZCUBIC*R*(T+273.15)/P
      IF(VG.LE.BB) THEN
      ICONV=3
      GO TO 400
      END IF
      IF(BB.LE.0.0) THEN
      ICONV=4
      GO TO 400
      END IF
      AW1=BW(J)*(DLOG((VG-BB)/(VL-BB))
     1 -P*(VG-VL)/(R*(T+273.15)))
      AW1=AW1*TR**(1.5)
      AW1=AW1/DLOG(VG*(VL+BB)/VL/(VG+BB))
      FAB(J)=AW1-AW
      PDELA=FAB(J)/AW
      IF(DABS(PDELA).LT.DBLE(0.001)) GO TO 300
      IF(J.LT.2) GO TO 100
      DFAB=FAB(J)-FAB(J-1)
      DBW=FAB(J)*(BW(J)-BW(J-1))/DFAB
      DB=(BW(J)-BW(J-1))/BW(J-1)
      IF(DABS(DB).LT.10.D-4) GO TO 300
C     LIMITING STEP LENGTH OF CHANGE OF B
      IF(DABS(DBW).GT.0.1) THEN
      DBW1=0.001
      DBW=DSIGN(DBW1,DBW)
      END IF
      BW(J+1)=BW(J)-DBW
100   CONTINUE
200   ICONV=5
      GO TO 400
300   ICONV=0
400   RETURN
      END

      SUBROUTINE SOAVE(I,T,AS,BS,ICONV)
C     THIS SUBROUTINE IS FOR MAKING CALCULATION OF PARAMETERS
C     OF EOS FOR THE COMPONENTS WHEN THE SYSTEM TEMPERATURE
C     EXCEEDS THEIR CRITICAL TEMPERATURES AND IS ACTUALLY
C     RARELY USED IN THIS PROJECT
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON /FIRST/ ID(10),TC(20),PC(20),W(20),WM(20),VSTR(20)
      COMMON /THIRD/ ITM,NCOMP,R,TOL
      C1=0.48+1.574*W(I)-0.176*W(I)*W(I)
      C2=(1.0+C1*(1.0-((T+273.15)/(TC(I)+273.15))
     1 **0.5))**2.0
```

```
      AS=0.42747*C2*R*R*(TC(I)+273.15)*
      1 (TC(I)+273.15)/PC(I)
      BS=0.08664*R*(TC(I)+273.15)/PC(I)
      ICONV=0
      RETURN
      END

      PROGRAM  STATIC
C     THIS PROGRAM IS FOR ISOTHERMAL FLASH, BP AND DP
C     CALCULATION. RKJZ'S, SOAVE'S AND CHUEH'S CORRELATIONS
C     ARE INCORPORATED IN THIS PROGRAM WHICH MAKE THE CALCULATION
C     CAN BE CARRIED OUT FOR MULTICOMPONENT MIXTURE CONTAINING
C     SUPERCRITICAL QUANTUM GAS, SUPERCRITICAL NORMAL GAS, NORMAL
C     HYDROCARBON, HEAVY HYDROCARBON AND COMPONENT FOR WHICH CRITICAL
C     PROPERTIES ARE UNVALAIBLE.
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION SUMF(120),FF(10)
      DIMENSION BW(120),FAB(120)
      COMMON /FIRST/ ID(10),TC(20),PC(20),W(20),WM(20),VSTR(20)
      COMMON /SECOND/ V(2,10),A(10),B(10),C(10,10),
      1 D(10,10),FUGAC(2,10)
      COMMON /THIRD/ ITM,NCOMP,R,TOL
      COMMON /FORTH/ T,GESB1,GESB2
      COMMON /FIFTH/ Z(10),X(2,10),CK(10)
      EXTERNAL FLASH,PROPTY,CRITIC,CHUEH
      EXTERNAL SOAVE,GUESK,CUBIC,PRESURE,RKJZ
C     IDENTIFY CALCULATION TYPE
      WRITE(*,230)
      READ(*,*) KIND
      IF(KIND.NE.3) THEN
      WRITE(*,240)
      READ(*,*) IADJUST,VAPEND
      END IF
C     INPUT CONTROL VARIABLE
      WRITE(*,250)
      READ(*,*) NCOMP,ITM,TOL,R
      DO 10 I=1,NCOMP
      WRITE(*,260) I
      READ(*,*) ID(I)
10    CONTINUE
C     START CALCULATION OF EOS PARAMETER FOR
C     PURE COMPONENT AND MIXTURE
      DO 20 I=1,NCOMP
      CALL PROPTY(I,TTC,PPC,WW,WWM,VVSTR)
      TC(I)=TTC
      PC(I)=PPC
      W(I)=WW
      WM(I)=WWM
      VSTR(I)=VVSTR
20    CONTINUE
      IF(IADJUST.EQ.1) THEN
      WRITE(*,290)
      READ(*,*) P
      ELSE IF(IADJUST.EQ.2) THEN
```

```
      WRITE(*,300)
      READ(*,*) T
      ELSE IF(IADJUST.NE.1.AND.IADJUST.NE.2) THEN
      WRITE(*,280)
      READ(*,*) T,P
      END IF
      DO 30 I=1,NCOMP
      WRITE(*,310) I
      READ(*,*) Z(I)
30    CONTINUE
      DO 40 I=1,NCOMP
      DO 40 J=1,NCOMP
      C(I,J)=0.0
      D(I,J)=0.0
40    CONTINUE
      WRITE(*,370)
      READ(*,*) IFIT,NUMCD
      IF(NUMCD.EQ.0) GO TO 80
      DO 50 N=1,NUMCD
      WRITE(*,380)
      READ(*,*) I,J,CD
      IF(IFIT.EQ.1) THEN
      C(J,I)=CD
      C(I,J)=CD
      ELSE IF(IFIT.EQ.2) THEN
      D(I,J)=CD
      D(J,I)=CD
      END IF
50    CONTINUE
      DO 70 I=1,NCOMP
      DO 60 J=1,NCOMP
      WRITE(*,390) I,J,C(I,J),D(I,J)
60    CONTINUE
70    CONTINUE
80    ITER=1
      IF(KIND.EQ.3) GO TO 90
      IF(IADJUST.EQ.1) THEN
      WRITE(*,320)
      READ(*,*) T
      ELSE IF(IADJUST.EQ.2) THEN
      WRITE(*,330)
      READ(*,*) P
      END IF
90    DO 120 I=1,NCOMP
      IF(ID(I).LE.10) THEN
      CALL CRITIC(I,T,TCQUN,PCQUN)
      CALL CHUEH(TCQUN,PCQUN,AT,BT,ICONV)
      VG=0.0
      VL=0.0
      GO TO 110
      END IF
      IF(ID(I).GT.10.AND.T.GE.TC(I)) THEN
      CALL SOAVE(I,T,AT,BT,ICONV)
      VG=0.0
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      VL=0.0
      GO TO 110
      END IF
      GESB1=0.06
      GESB2=0.07
100   CALL RKJZ(I,AT,BT,VG,VL,ICONV3)
      IF(ICONV3.NE.0) THEN
      WRITE(*,480) I
      READ(*,*) GESB1, GESB2
      GO TO 100
      END IF
110   A(I)=AT
      B(I)=BT
      V(1,I)=VG
      V(2,I)=VL
120   CONTINUE
      IF(ITER.GT.1) GO TO 170
      WRITE(*,420)
      READ(*,*) IGUESK
      IF(IGUESK.EQ.1) THEN
      CALL GUESK(T,P,CK)
      GO TO 150
      ELSE IF(IGUESK.EQ.2) THEN
      GO TO 130
      END IF
130   DO 48 I=1,NCOMP
      WRITE(*,430) I
      READ(*,*) CK(I)
140   CONTINUE
150   DO 160 I=1,NCOMP
      WRITE(*,440) I,CK(I)
160   CONTINUE
      WRITE(*,450)
      READ(*,*) ICHANGE
      IF(ICHANGE.EQ.1) GO TO 130
C     START FLASH CALCULATION
170   CALL FLASH(T,P,FV,KIND3,ICN,IFLASH)
      IF(KIND3.NE.0) GO TO 200
      IF(ICN.EQ.1) THEN
      WRITE(*,490)
      ELSE IF(ICN.EQ.2) THEN
      WRITE(*,500)
      ELSE IF(ICN.EQ.3) THEN
      WRITE(*,510)
      END IF
      IF(KIND.EQ.3) GO TO 180
C     PERFORM BP OR DP CALCULATION BY ADJUSTING ITERATIVE VARIABLE
      WRITE(*,270) ITER,T,P,FV,IADJUST
      WRITE(*,460)
      READ(*,*) ICNPXT
      IF(ICNPXT.NE.1) GO TO 180
      WRITE(*,470)
      READ(*,*) DPXT
      IF(IADJUST.EQ.1) THEN
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```
      T=T+DPXT
      ELSE IF(IADJUST.EQ.2) THEN
      P=P+DPXT
      END IF
      ITER=ITER+1
      IF(ITER.GT.(ITM+100)) GO TO 200
      IF(IADJUST.EQ.1) GO TO 90
      IF(IADJUST.EQ.2) GO TO 170
C     OUTPUT CALCULATION RASULTS
180   WRITE(*,340)
      WRITE(*,350) KIND,IADJUST,IGUESK,NCOMP,T,P,FV,IFIT
      DO 70 I=1,NCOMP
      WRITE(*,360) I,Z(I),X(1,I),X(2,I),CK(I)
190   CONTINUE
      GO TO 210
200   WRITE(*,370) KIND3
210   DO 85 I=1,NCOMP+1
      WRITE(*,410) I,A(I),B(I),V(1,I),V(2,I)
220   CONTINUE
      STOP
230   FORMAT(2X,'KIND    = 1   BP CALCULATION'/
      1 2X,'KIND    = 2   DP CALCULATION'/
      2 2X,'KIND    = 3   FL CALCULATION'/
      3 2X,'READ KIND'//)
240   FORMAT(2X,'IADJUST = 1   TEMP ADJUSTED'/
      4 2X,'IADJUST = 2   PRER ADJUSTED'/
      5 2X,'READ IADJUST AND VAPEND'//)
250   FORMAT(2X,'READ NCOMP,ITM,TOL,R'//)
260   FORMAT(2X,'I = ',I5/
      6 2X,'READ ID'//)
270   FORMAT(2X,'ITER =',I5,2X,'T =',D10.4,2X,'P =',D10.4,
      6 2X,'FV =',D10.3,2X,'IAJST =',I5)
280   FORMAT(2X,'READ T , P'//)
290   FORMAT(2X,'READ PRESSURE'/)
300   FORMAT(2X,'READ TEMPERATURE'/)
310   FORMAT(2X,'I = ',I5/
      7 2X,'READ Z'//)
320   FORMAT(2X,'READ GUESS T VALUE'//)
330   FORMAT(2X,'READ GUESS P VALUE'//)
340   FORMAT(/2X,'CALCULATION SUCCESSED'/)
350   FORMAT(2X,'KIND    = ',I5/
      1 2X,'IADJUST = ',I5/
      2 2X,'IGUESK  = ',I5/
      3 2X,'NCOMP   = ',I5/
      4 2X,'TEMP    = ',D10.5/
      5 2X,'PRESURE = ',D10.5/
      6 2X,'FV      = ',D10.5/
      7 2X,'IFIT    = ',I5//)
360   FORMAT(2X,'I =',I5,2X,'Z =',D10.5,2X,'Y =',D10.5,
      6 2X,'X =',D10.5,2X,'K =',D10.5)
370   FORMAT(2X,'CALCULATION FAILED'/
      6 2X,'KIND3 = ',I5)
380   FORMAT(2X,'READ IFIT'/
      1 2X,'READ NUMBER OF NON-ZERO C OR D VALUES'//)
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390     FORMAT(2X,'READ I,J,CD-VALUE'//)
400     FORMAT(2X,'I= ',I5,1X,'J =',I5,1X,'C =',D11.4,1X,'D =',D11.4)
410     FORMAT(2X,'I =',I5,2X,'A =',D10.5,2X,
        7 'B =',D10.5,2X,'VG =',D10.5,2X,'VL =',D10.5)
420     FORMAT(2X,'READ IGUESK'/2X,'IGUESK=1:CALL GUESK'/
        8 2X,'IGUESK=2:INPUT K'//)
430     FORMAT(2X,'I =',I5,2X,'READ K VALUE'//)
440     FORMAT(2X,'I =',I5,2X,'K =',D10.5)
450     FORMAT(2X,'READ ICHANGE'/2X,'ICHANGE=0:NO CHANGE'/
        9 2X,'ICHANGE=1:CHANGE K BY INPUT DATA OF K'//)
460     FORMAT(2X,'READ ICNPXT'/2X,'ICNPXT=1 : CHANGE DPXT'/
        1 2X,'ICNPXT NE 1 : TERMINATING CALCULATION'//)
470     FORMAT(2X,'READ DPXT'//)
480     FORMAT(2X,'I = ',I5/2X,'READ GESB1 GESB2:'/)
490     FORMAT(2X,'TWO PHASE REGION'/)
500     FORMAT(2X,'SINGLE PHASE REGION'/)
510     FORMAT(2X,'CRITICAL POINT'/)
520     FORMAT(2X,'READ GUESSED T'/)
530     FORMAT(2X,'READ GUESSED P'/)
        END
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VITA

Huaping Chen

Candidate for the Degree of

Master of Science

Thesis: HYDROGEN-HEAVY HYDROCARBON PHASE EQUILIBRIUM AND MODELING OF A RECIRCULATION REACTOR

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Suchou, Jiangsu Province, November 6, 1962.

Education: Graduate from Suchou 22nd High School in June 1980; received Bachelor of Engineering Degree in Chemical Engineering from East China Institute of Chemical Technology in June, 1985; completed requirements for the Master of Science degree at Oklahoma State University in May, 1990.

Professional Experience: Research Assistant, School of Chemical Engineering, Oklahoma State University, January, 1988, to June, 1988; Teaching Assistant, School of Chemical Engineering, Oklahoma State University, August, 1988, to May, 1990.